



Learning and Labor.

LIBRARY

OF THE

University of Illinois.

CLASS.

BOOK.

VOLUME.

540

H59

Books are not to be taken from the Library.

Accession No.







Return this book on or before the  
*Latest Date* stamped below. A  
charge is made on all overdue  
books.

U. of I. Library


NOV 4 - 1935

JUL - 7 '36

DEC 13 1940

JUL - 6 1943

8057-S



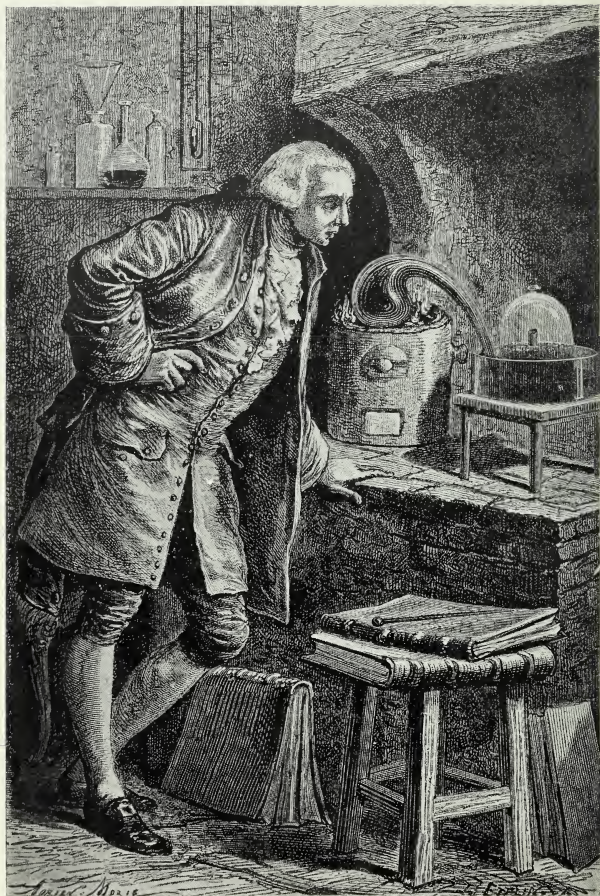
Digitized by the Internet Archive  
in 2017 with funding from  
University of Illinois Urbana-Champaign Alternates

Ricordiamoci in grazia, che il cercar  
la costituzione del mondo è de' maggiori  
e de' più nobili problemi, che sieno in  
natura.

GALILEO GALILEI,

*Gj. II., Sistemi.*





LAVOISIER.

EXPERIMENTUM CRUCIS.

INTRODUCTION  
TO  
GENERAL CHEMISTRY.  
A GRADED COURSE OF  
ONE HUNDRED LECTURES

BY  
GUSTAVUS DETLEF HINRICHS, M.D., LL.D.

HONORARY AND CORRESPONDING MEMBER OF SCIENTIFIC SOCIETIES IN FRANCE,  
GERMANY AND THE UNITED STATES; PROFESSOR OF CHEMISTRY,  
ST. LOUIS COLLEGE OF PHARMACY.

---

WITH AN  
ATLAS OF EIGHTY PLATES,

REPRESENTING CHEMISTS, INSTITUTIONS, PRIME MATERIALS,  
CRYSTALS, DIAGRAMS AND APPARATUS; AND ILLUSTRATIONS IN THE TEXT.

---

ST. LOUIS, MO., U. S.

CARL GUSTAV HINRICHS, PUBLISHER.

NEW YORK AND LEIPZIG, LEMCKE AND BUECHNER.  
LONDON, H. GREVEL & Co. PARIS, H. LE SOUDIER.

1897.

Entered According to Act of Congress, in the year 1897, by  
GUSTAVUS HINRICHS,  
In the Office of the Librarian of Congress, at Washington.

---

ALL RIGHTS RESERVED BY THE AUTHOR.

---

PHOTO-ENGRAVINGS BY SANDERS ENGRAVING CO.,  
ST. LOUIS, MO.

---

PRINTED BY R. P. STUDLEY & CO.,  
ST. LOUIS, MO.

540  
H 59

*Remote  
Storage*

— TO —

CHARLES FRIEDEL,

MEMBER OF THE INSTITUTE OF FRANCE,

PROFESSOR OF THE FACULTY OF SCIENCES,

CONSERVATOR OF THE MINERALOGICAL MUSEUM  
OF THE NATIONAL SCHOOL OF MINES, OF PARIS,

THIS VOLUME

IS DEDICATED BY

THE AUTHOR.

37761





MONSIEUR CHARLES FRIEDEL,

MEMBRE DE L' INSTITUT,

PARIS, FRANCE.

MY DEAR SIR :

The Introduction to General Chemistry herewith most respectfully dedicated to you, is intended to give the student a first view of the broad field of science that has been enriched by your researches, and to serve as a supplement to existing treatises of our science.

To you, the form of a crystal, the synthesis of a mineral and the formation of a new series of organic compounds have been chemical problems of equal importance. Hence the solution of every single problem by your hands has enriched chemistry with a new principle as broad as the horizon of your mind.

Thus, when you made the ancient dwarfs of the mountain speak, the crystal revealed to you its true composition. Upon this you built an organic chemistry of the deep, of which that of air and sun is like the spirit.

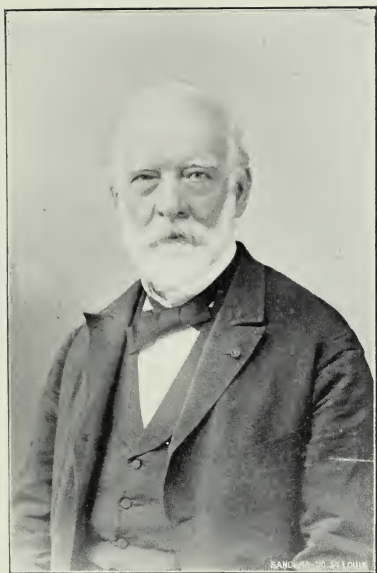
Your official trusts have been as broad as your chemical work. The magnificent collection of minerals at the École des Mines, and Organic Chemistry at the Sorbonne, have been equally benefitted by that breadth of mind which the specialist cannot even understand.

Your recent establishment of Les Actualités Chimiques makes all chemists of the world your debtors. The Great Chemist of the North first sacrificed his time to such a task, eighty years ago. For a while, his creation was continued in another country, by the kindred minds of a Liebig and a Woehler. But with modern Byzantinism, the Jahresberichte have depreciated in character even more than they have increased in bulk. You happily have found a form in which the thought of Berzelius arises to new life for the good of science.

That your Colleague, Professor Schuetzenberger of the Collège de France, under your presidency, has delivered a Lecture on work of mine to the chemists of Paris, at the Sorbonne, and that you have opened your new Review with a full report thereof, is acknowledged as a great distinction with gratitude by

THE AUTHOR.

St. Louis, Mo., U. S., March 15, 1897.



Je vous prie d'agréer Monsieur  
et des Collèges l'assurance de  
mon cordial bienvenue et  
mon meilleur organe pour votre santé.  
Friede

Je me suis proposé d'embrasser, dans ma publication, la science tout entière; mon livre sera complet, quand au but; il ne sera élémentaire que par le choix des méthodes.

FRANÇOIS ARAGO,

Astr.-pop. T. I., 1854.

## PREFACE.

---

This work embodies the experience of nearly forty years behind the Lecture Table. I have addressed fully ten thousand students in the aggregate.

For a century, our chemical text-books have been modelled on one pattern. They all begin with general principles that require advanced knowledge to be understood. The student is first directed to observe that which he cannot see, and to comprehend that which it took old chemists centuries to learn. At the same time, that which is common and of great practical importance, is withheld till late in the course or entirely omitted. Many gases that were of special interest a century ago, are still made prominent, though of no significance at present, while the instructive and useful gasometric processes are given no place.

A reformation seems necessary. It has been attempted in this book. The entire science is presented in a strictly graded course. The principal points are determined in the order of their historic growth. The discovery of oxygen is not presented until its necessity can be understood; it comes as the dramatic event that it actually was in history. The atomic theory comes last, and is here carried to completion.

The real authors of chemistry are the chemists that created the science. Hence the portraits of the makers precede their work. The other parts of the Atlas are equally essential. The pictorial representation of the prime materials we would like to have increased largely.

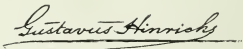
The present is the Lecture Course exclusively. It is supplemented by a Laboratory Course, the guide for which it is our intention to issue in another year. The lecture is not the place for details on processes and apparatus. It is as impossible to teach as it is to learn such details in the lecture hall. At the laboratory stand such knowledge is acquired almost without an effort.

The plates of apparatus are largely suggestive of what is presented at each lecture. The experiments are sufficiently indicated in the text. Neither apparatus, nor experiment, should ever be introduced simply for show or amusement. They are means to an end, namely the establishment of chemical facts and principles.

This book does not aim to be a systematic treatise on compounds. Of such books there are enough. The best by far is the *Traité* of Troost, (11th edit., Paris, 1895); it is a masterpiece of completeness and condensation; it gives a maximum of chemistry in a minimum of space.

The selection of topics, and their order of succession, has been to me a matter of much study and consideration for many years. The text has also been most carefully written and re-written. It has been my constant aim to make the text concise and clear. Each lecture deals with a single, definite topic. It is treated as a subject by itself. The best French writers have been my models of style.

But the work is before the reader and the student. I respectfully submit it to their consideration.



SUGGESTION: In a first course it is advisable to omit the more difficult quantitative inorganic part (Lectures 38 to 51) till Lecture 80 in organic chemistry has been heard. After that, and perhaps a review, the more difficult quantitative parts can be taken with greatest advantage.

# CONTENTS.

---

TEXT OF ONE HUNDRED LECTURES.

---

## INORGANIC CHEMISTRY

---

### I. CHEMICAL AGENCIES:

1, Chemistry and Al Kemi. 2, Weight and Measure. 3, Solids and Fluids. 4, Fusing and Boiling. 5, Furnace and Blowpipe.

### II. METALS AND MINERALS:

6, Metals, old and new. 7, Calcination and Reduction. 8, Alloys and Amalgams. 9, Ores and Cleavage. 10, Crystal Gems. 11, Crystal Stones. 12, Rocks and Veins. 13, Salts and Spirits. 14, Solution and Crystallization. 15, Crystal Description.

### III. CHEMICAL REACTIONS:

16, Marble and Fixed Air. 17, Zinc and Inflammable Air. 18, Substitution by Solution. 19, Solution of Silver and Gold. 20, Reduction in the Wet Way. 21, Sulphur and Sulphides. 22, Hydrogen Sulphide and the Metals. 23, Iodine and Iodides. 24, Acidimetry and Alkalimetry. 25, Neutralization and Calorization. 26, Flux and Glass. 27, Metals and Radicals. 28, Chemical Reactions.

### IV. COMBUSTION:

29, Combustion and Phlogiston. 30, Combustion and Oxygen. 31, Oxide and Radical. 32, Analysis of the Air. 33, Nitrogen, Phosphorus and Argon.

### V. ELECTROLYSIS:

34, Battery and Dynamo. 35, Qualitative Electrolysis. 36, Applied Electrolysis. 37, Equivalent and Electricity.

### VI. CHEMICAL FORMULÆ:

38, Equivalent and Volume. 39, Equivalent and Heat. 40, Atoms and Molecules. 41, Elements and Compounds. 42, Allotropy and Isomery. 43, Binaries and Ternaries. 44, Formula and Compound.

### VII. CHEMICAL ANALYSIS:

QUANTITATIVE: 45, Purity and Strength. 46, The Analytical Balance. 47, Specific Gravity Methods. 48, Analysis by Dissociation. 49, Gasometric Analysis. 50, Volumetric Analysis. 51, Gravimetric Analysis.

QUALITATIVE: 52, Spectrum Analysis. 53, Dry Way Analysis. 54, Wet Way Analysis of Bases. 55, Wet Way Analysis of Acids. 56, Recognition of Specimens.

# ORGANIC CHEMISTRY.

---

## VIII. ORGANIC PRIME MATERIALS:

VEGETABLE: 57, Organic Prime Materials. 58, Sugar and Wine. 59, Fats and Oils. 60, Flower and Fragrance. 61, Indigo and Madder. 62, Balsam and Resin. 63, Vegetable Acids. 64, Vegetable Bases. 65, Neutral Principles. 66, Starch and Fiber.

ANIMAL: 67, Milk and Butter. 68, Flesh and Blood. 69, Bone and Sinew. 70, Animal and Plant. 71, Fermentation and Life.

FOSSIL: 72, Petroleum and Coal. 73, Gas and Tar. 74, Phenol and Aniline. 75, Bone Oil and Wood Spirits.

## IX. CHEMICAL TRANSFORMATIONS:

76, Starch, Sugar and Glucose. 77, Alcohol and Ethers. 78, Fats and Soaps. 79, Nitro-Glycerin and Gun-Cotton. 80, Chloracetic Acid and Chloral.

## X. CHEMICAL CONSTITUTION:

81, Proximate and Ultimate Analysis. 82, Empirical and Molecular Formulæ. 83, Radical and Structural Formulæ. 84, Polymeric and Isomeric Compounds. 85, Right- and Left-Handed Compounds. 86, Tetrahedron and Benzol Ring. 87, Alcoholic Compounds. 88, Aromatic Compounds. 89, Complex Compounds. 90, Organic Synthesis.

## XI. ATOM-MECHANICS:

91, The Atom World. 92, Prismatic Atoms and Boiling. 93, Atom Linkage and Fusing. 94, Atom Volume. 95, Isomeric Atoms. 96, Atomic Rotation. 97, Atomic Libration. 98, Atomic Crystals. 99, Atomic Weights. 100, The Atomic Composition of the Elements.

---

## ERRATA.

LECT. 24. Sect. 5: For 5 cc read 50 cc; for 7 in line 5 read 31; Sect. 12, line 1, for proportion read preparation. LECT. 25. S. 6, L. 3: for ammonia read ammonium; S. 10, L. 6: from calcium, read for calcium. LECT. 32. S. 2, L. 5: For hydrometer, read hygrometer. LECT. 33. S. 10, L. 2: Raleigh, read Rayleigh. LECT. 37. S. 11, L. 7: The —ous, read the anomalous. LECT. 40. S. 7, L. 4: For Na 27 read Na 23. LECT. 49. S. 11, L. 9: For  $2 \text{ Ca O Cl} = 183$ , read  $\text{Ca (O Cl)}_2 = 143$ ; L. 10, for 7.629 read 5.96. LECT. 51. S. 9, L. 3: Indicated read indicator. LECT. 60. S. 9, L. 6: Add B 160. LECT. 84. S. 2, L. 3: terrible read terribly. LECT. 86. S. 3, L. 5, admirable read admirably.



# THE STUDENT'S ATLAS.

---

## I. CHEMISTS AND INSTITUTIONS:

CHEMISTS: 17, In Old Kemi.—A Modern Temple of Chemistry (Leipzig). 18, Galileo Galilei. 19, Lavoisier. 20, Huyghens. 21, Boyle. 22, Berzelius. 23, Liebig. 24, Bunsen. 25, Dumas. 26, Faraday. 27, Berthelot. 28, Haidinger. 29, Padre Secchi. 30, Lemery; Van Helmont. 31, Pasteur; Volta. 32, Berthollet; Dalton. 33, Richter; Stas. 34, Mitscherlich; Hofmann. 35, Kirchhoff; Kekulé. 36, Claude Bernard; Moissan. 37, Chevreul; Court of the Institut.

INSTITUTIONS: 38, Palace of the Institute of France; Ante-room of the Academy of Sciences. 39, Meeting Room of the Academy; The Institute of France, see pp. 37, 38, 39, 42. 39, Balance Room at Breteuil (International Bureau of Weights and Measures). 40, Chemical Lecture Halls; Gratz, Paris. 41, Chemical Laboratories; Giessen; Leipzig. 42, Chemical Research Library; Secretary Berthelot's Room in the Palace of the Institute. 43, A page from the Saint Mark Manuscript.

## II. PRIME MATERIALS:

44, Galileo's Moons of Jupiter; Meteorite Field in Iowa. 45, Amana Meteorites, Hinrichs' Collections. 46, Gems (models). 47, Veins. 48, Coal; Gold. 49, Vanilla; Milk. 50, Sea Salt; Rock Salt. 51, Cryolite; Marble. 52, Cinchona; Magnetite.

## III. THE CRYSTAL WORLD:

53, Microphotographs of Snow Crystals; Alexandrite Crystals, Siberia. 54, Cubical Crystals, Romé de l' Isle. 55, Calcite Crystals, Haüy. 56, Beryl; Corundum. 57, Hematite. 58, Magnetite. 59, Cuprite; Garnet. 60, Zircon. 61, Topaz. 62, Topaz; Alexandrite. 63, Pyroxene. 64, Orthoclase; Anorthite. 65, Quartz; Calcite. 66, 67, The Principal Crystal Forms, according to Von Kobell. 68, Blackboard Sketches of Common Crystals, and Student's Goniometer. 69, Sulphur Crystals (with their axes).

#### IV. DIAGRAMS:

70, Solubility in Water, Gay-Lussac. 71, Solubility in Water, Etard. 72, Spectra of the Light Metals, Bunsen and Kirchhoff. 73, Chemical Reactions, Dry Way and Wet Way. 74, Boiling and Fusing Points of Paraffins. 75, Boiling Points of Acids, Alcohol, etc., (log. a). 76, Terminal Substitution, complex. 77, Terminal Substitution, simple. 78, Boiling Point of Isomeric Ethers. 79, Stas' Determination of Silver Nitrate. 80, Hinrichs' System of the Elements, showing their Composition.

#### V. SUPPLEMENT:

385, Cleopatra's Chrysopoeia, Berthelot; Chemical Valence, Hinrichs', 1867. 386, Weight and Measure. 387, Gasometric Apparatus. 388, Gas Manipulation. 389, Distilling and Extracting Apparatus; Professor's Stand, Chemical Laboratory, St. Louis College of Pharmacy. 390, Micrographs of Ferments. 391, Hinrichs' Chemical Elements, 1867. 392, The Dodecahedron; The Pyritohedron. Haüy, Origin of Secondary Forms. 393, Daubrée. 394, Structure and Properties. The Paraffins. 395, Structure and Libration. Benzol. 396-7. Hinrichs' System of the Elements, 1867 and 1897. 398, Origin of the "Periodic Law." Atomic Weights, Diamond Standard. 399, Half a page from Hinrichs' Programme der Atom Mechanik, 1867. 400, A Look-Out to the Old Pastures (67, 1).

#### PORTRAITS IN THE TEXT:

Agricola. Daubrée. Lavoisier in Prison under the Reign of Terror (full page). Priestly. Scheele. Woehler.



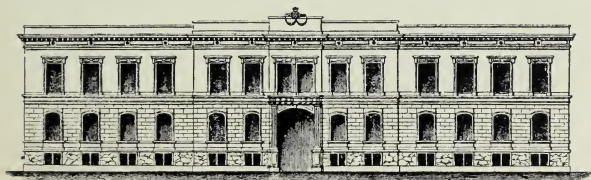
IN OLD KEMI.

---

# THE STUDENT'S ATLAS.

I. CHEMISTS AND INSTITUTIONS.

---



A MODERN TEMPLE OF CHEMISTRY



GALILEO GALILEI.



LAVOISIER.



HUYGHENS.



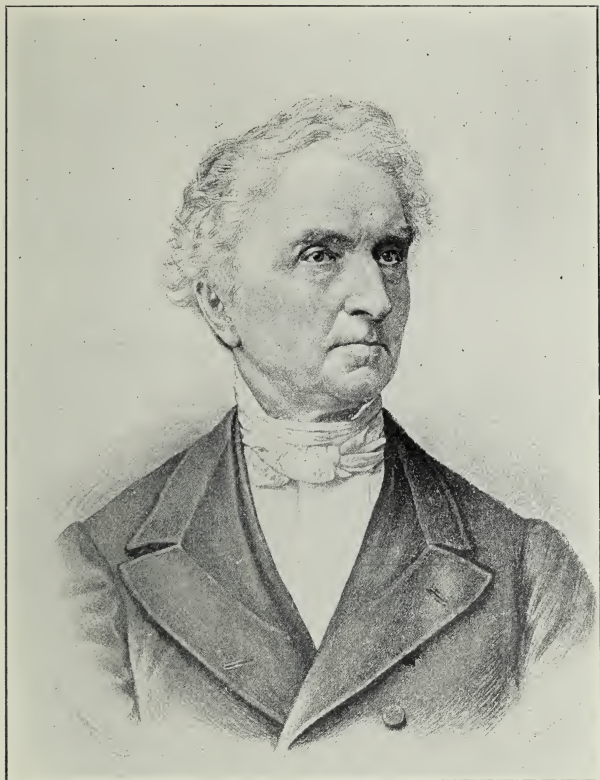


BOYLE.

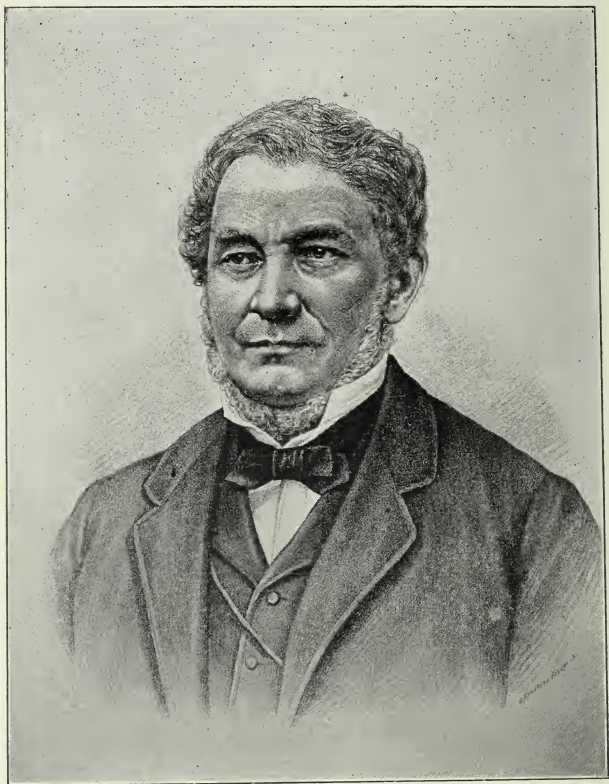


BERZELIUS.

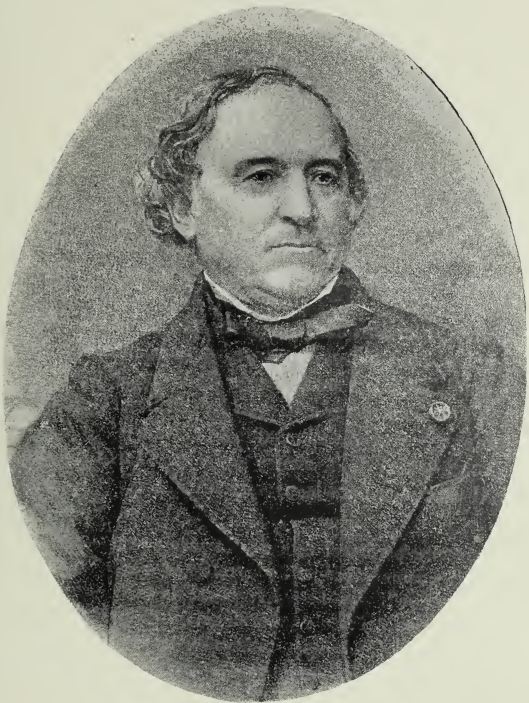




LIEBIG.



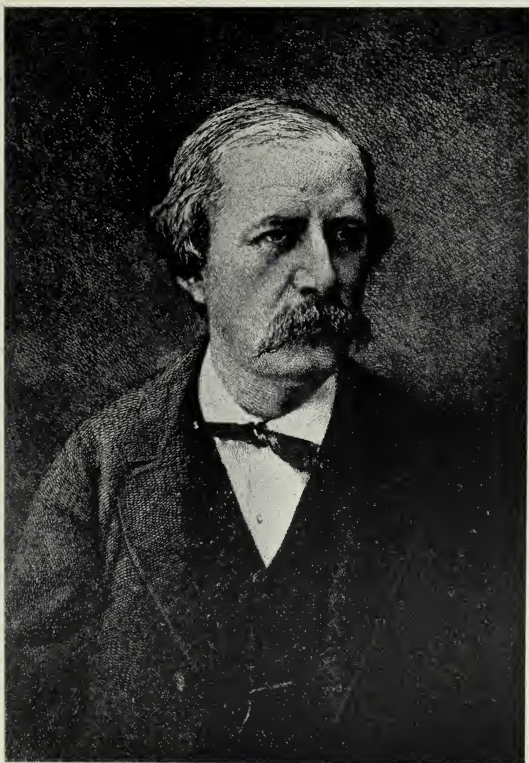
BUNSEN.



DUMAS.

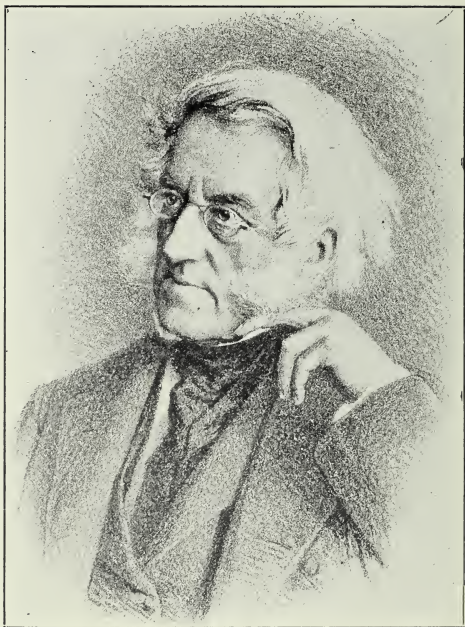


FARADAY.



BERTHELOT.

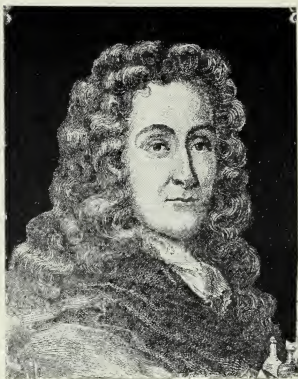




HAIDINGER.



P. SECCHI.

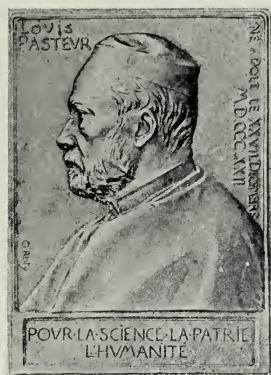


LEMERY.



VAN HELMONT.

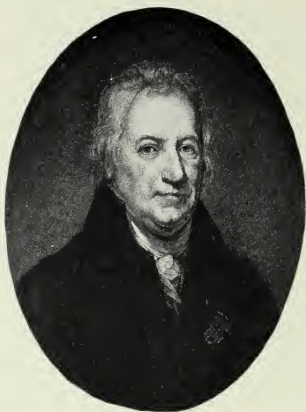




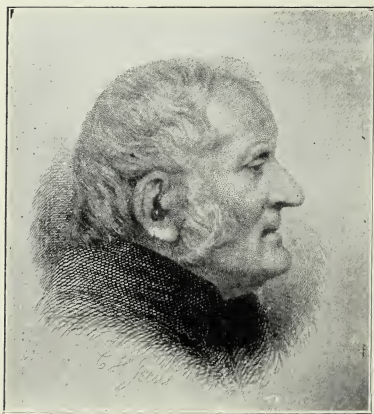
PASTEUR.



VOLTA.



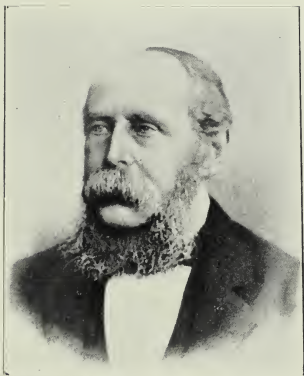
BERTHOLLET.



DALTON.



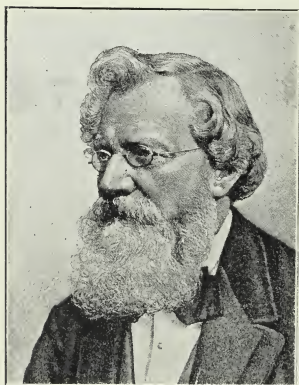
RICHTER.



STAS.



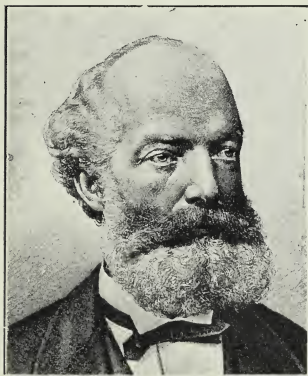
MITSCHERLICH.



HOFMANN.



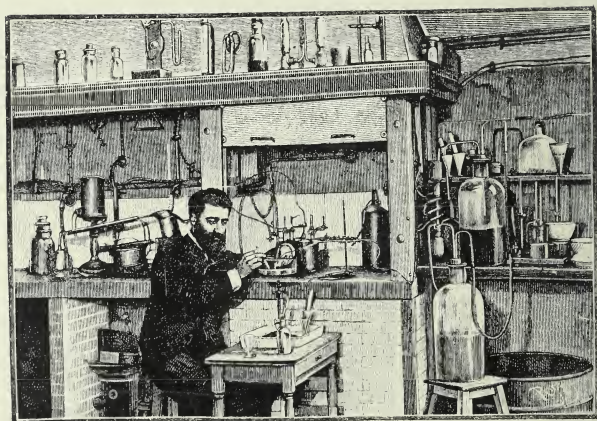
KIRCHHOFF.



KEKULÉ.



CLAUDE BERNARD.



MOISSAN.

ISOLATING FLUORINE IN THE SCHOOL OF PHARMACY, PARIS.



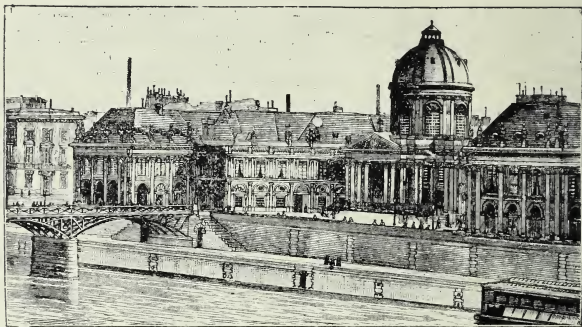


COURT OF THE INSTITUTE.

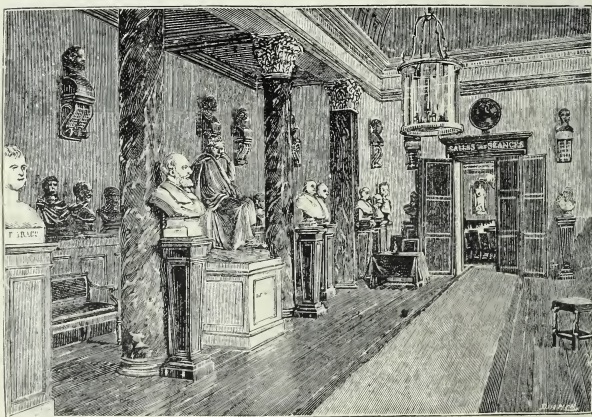


CHEVREUL,

AT THE AGE OF ONE HUNDRED YEARS.

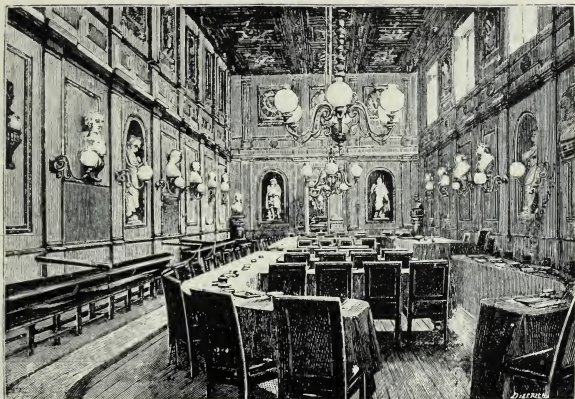


PALACE OF THE INSTITUTE.

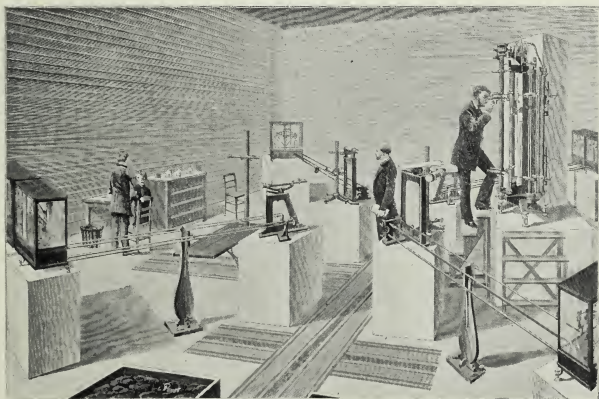


ANTEROOM OF THE ACADEMY.

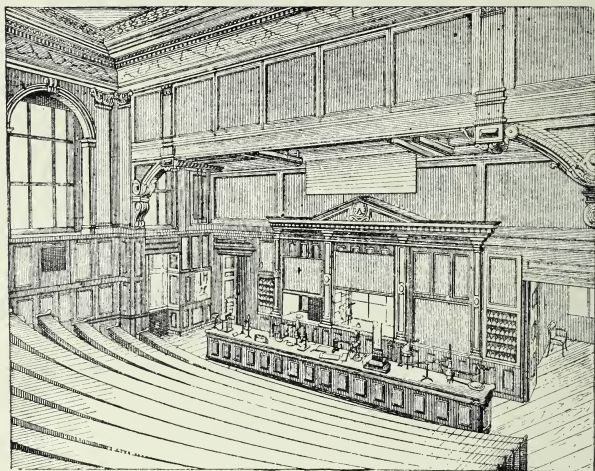




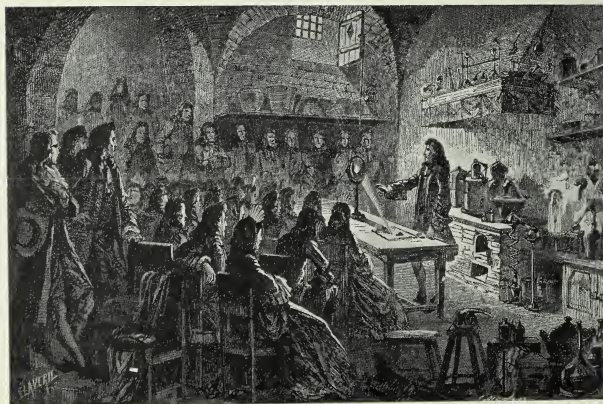
MEETING ROOM OF THE ACADEMY.



BALANCE ROOM AT BRETEUIL.



CHEMICAL LECTURE HALL, UNIVERSITY OF GRATZ.



LECTURE BY LEMERY, PARIS, 1680.



LIEBIG'S LABORATORY, GIESSEN.



IN KOLBE'S LABORATORY, LEIPZIG.





BERTHELOT,  
IN HIS ROOM AT THE PALACE OF THE INSTITUTE.

100126X 100127X

*Xristianina*

B ΧΡΥΣΟΥ ΜΕΤΑΛΑ ΘΥ      Η ΚΡΟΝΟΣ ΦΑΙΝΟΝ ΛΙΒΕ  
 ΔΥΤΤΟΚΕΚΛΥΜΕΝ      ΖΕΥΤ ΦΑΙΤΩΝ ΝΔΕΚΤΟC

ХРҮСН ЛЕКТРОН

Χρυσόκολλα ρ αφροσίτη φασφορίχαλκοι

22 ~~α~~αλλ' αὐτὸς ἔστιν ὁ  
 23 ~~α~~αὐτὸς

[illegible]

④ ἀρχιερῆς ἱεροῦ  
 ⑤ ἀρχιερῆς ἱεροῦ

6. 2p r r p o r π e t a λ 2  
 7. 2p r r p o x p x c o x o z d 4

22. 23.  
 24. 25.  
 26. 27.  
 28. 29.  
 30. 31.  
 32. 33.  
 34. 35.  
 36. 37.  
 38. 39.  
 40. 41.  
 42. 43.  
 44. 45.  
 46. 47.  
 48. 49.  
 50. 51.  
 52. 53.  
 54. 55.  
 56. 57.  
 58. 59.  
 60. 61.  
 62. 63.  
 64. 65.  
 66. 67.  
 68. 69.  
 69. 70.  
 70. 71.  
 71. 72.  
 72. 73.  
 73. 74.  
 74. 75.  
 75. 76.  
 76. 77.  
 77. 78.  
 78. 79.  
 79. 80.  
 80. 81.  
 81. 82.  
 82. 83.  
 83. 84.  
 84. 85.  
 85. 86.  
 86. 87.  
 87. 88.  
 88. 89.  
 89. 90.  
 90. 91.  
 91. 92.  
 92. 93.  
 93. 94.  
 94. 95.  
 95. 96.  
 96. 97.  
 97. 98.  
 98. 99.  
 99. 100.  
 100. 101.  
 101. 102.  
 102. 103.  
 103. 104.  
 104. 105.  
 105. 106.  
 106. 107.  
 107. 108.  
 108. 109.  
 109. 110.  
 110. 111.  
 111. 112.  
 112. 113.  
 113. 114.  
 114. 115.  
 115. 116.  
 116. 117.  
 117. 118.  
 118. 119.  
 119. 120.  
 120. 121.  
 121. 122.  
 122. 123.  
 123. 124.  
 124. 125.  
 125. 126.  
 126. 127.  
 127. 128.  
 128. 129.  
 129. 130.  
 130. 131.  
 131. 132.  
 132. 133.  
 133. 134.  
 134. 135.  
 135. 136.  
 136. 137.  
 137. 138.  
 138. 139.  
 139. 140.  
 140. 141.  
 141. 142.  
 142. 143.  
 143. 144.  
 144. 145.  
 145. 146.  
 146. 147.  
 147. 148.  
 148. 149.  
 149. 150.  
 150. 151.  
 151. 152.  
 152. 153.  
 153. 154.  
 154. 155.  
 155. 156.  
 156. 157.  
 157. 158.  
 158. 159.  
 159. 160.  
 160. 161.  
 161. 162.  
 162. 163.  
 163. 164.  
 164. 165.  
 165. 166.  
 166. 167.  
 167. 168.  
 168. 169.  
 169. 170.  
 170. 171.  
 171. 172.  
 172. 173.  
 173. 174.  
 174. 175.  
 175. 176.  
 176. 177.  
 177. 178.  
 178. 179.  
 179. 180.  
 180. 181.  
 181. 182.  
 182. 183.  
 183. 184.  
 184. 185.  
 185. 186.  
 186. 187.  
 187. 188.  
 188. 189.  
 189. 190.  
 190. 191.  
 191. 192.  
 192. 193.  
 193. 194.  
 194. 195.  
 195. 196.  
 196. 197.  
 197. 198.  
 198. 199.  
 199. 200.  
 200. 201.  
 201. 202.  
 202. 203.  
 203. 204.  
 204. 205.  
 205. 206.  
 206. 207.  
 207. 208.  
 208. 209.  
 209. 210.  
 210. 211.  
 211. 212.  
 212. 213.  
 213. 214.  
 214. 215.  
 215. 216.  
 216. 217.  
 217. 218.  
 218. 219.  
 219. 220.  
 220. 221.  
 221. 222.  
 222. 223.  
 223. 224.  
 224. 225.  
 225. 226.  
 226. 227.  
 227. 22

22 χαλκος υπριος - 2  
 23 κασιτηριος  
 24 κασιτηριου τη

88 χαλκοϋτη  
 89 χαλκοϋρηνη

χαλκον πεταλα  
 χαλκον πεταλα

Ⲫⲕ ϭⲁⲗⲕⲟⲩⲕⲉⲕⲁⲩⲁⲛⲟⲩ ⲛⲁⲗⲕⲟⲩⲕⲉⲕⲁⲩⲁⲛⲟⲩ

ο ι ο ο χ α λ κ ο υ  
 λ ο ι ο ο χ α λ κ ο ς

Σ Ν Ε Φ Ε λ Η  
 Χ

222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294 295 296 297 298 299 300 301 302 303 304 305 306 307 308 309 310 311 312 313 314 315 316 317 318 319 320 321 322 323 324 325 326 327 328 329 330 331 332 333 334 335 336 337 338 339 340 341 342 343 344 345 346 347 348 349 350 351 352 353 354 355 356 357 358 359 360 361 362 363 364 365 366 367 368 369 370 371 372 373 374 375 376 377 378 379 380 381 382 383 384 385 386 387 388 389 390 391 392 393 394 395 396 397 398 399 400 401 402 403 404 405 406 407 408 409 410 411 412 413 414 415 416 417 418 419 420 421 422 423 424 425 426 427 428 429 430 431 432 433 434 435 436 437

$\theta \approx 112.1^\circ$

1. сидрохризма  $\delta$  сидрохризон  
 2. сидрохризма  $\delta$  сидрохризон

$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ 0 & 1 \end{pmatrix}$

Κυριανός                      Φε ἀφροελληνόν

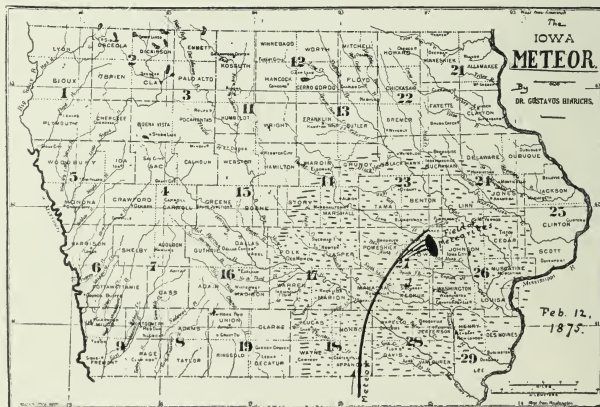
SAINT MARK MANUSCRIPT, FROM BERTHELOT.



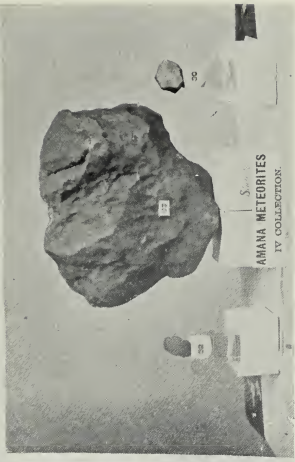
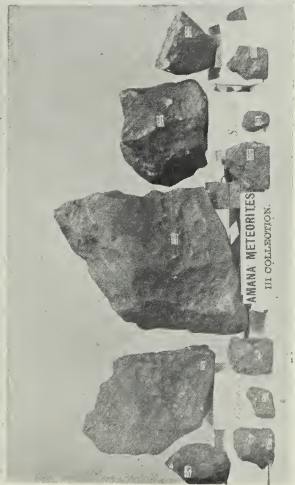
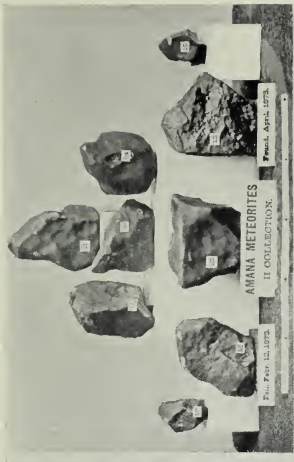
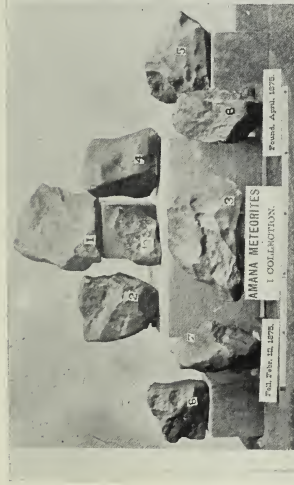
GALILEO SHOWING THE MOONS OF JUPITER TO THE  
SENATORS OF VENICE.

# THE STUDENT'S ATLAS.

## II. PRIME MATERIALS.



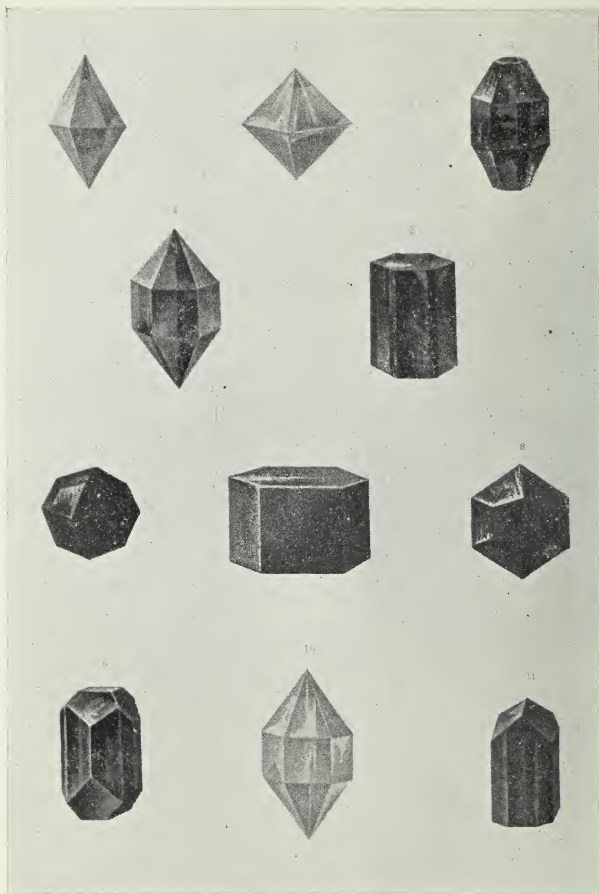
THE GREAT IOWA METEOR, FEBRUARY 12, 1875.



# AMANA METEORITES. Hinrichs' Collections.

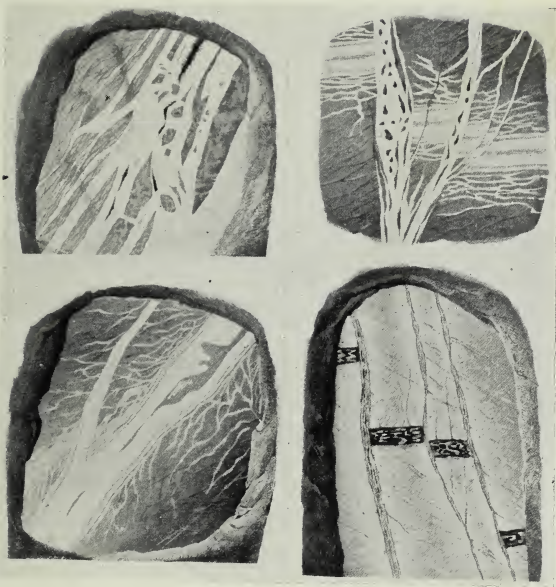
- |                 |                              |
|-----------------|------------------------------|
| 1. PARIS.       | 11. ST. PETERSBURG.          |
| 2. LONDON.      | 13. BRUSSELS.                |
| 3. CHRISTIANIA. | 14. HARLEM.                  |
| 4. VIENNA.      | 15. PARIS (SECOND SPECIMEN). |
| 5. COPENHAGEN   |                              |
- THESE METEORITES WERE PRESENTED IN 1875 BY THE AUTHOR TO THE MUSEUMS NAMED.





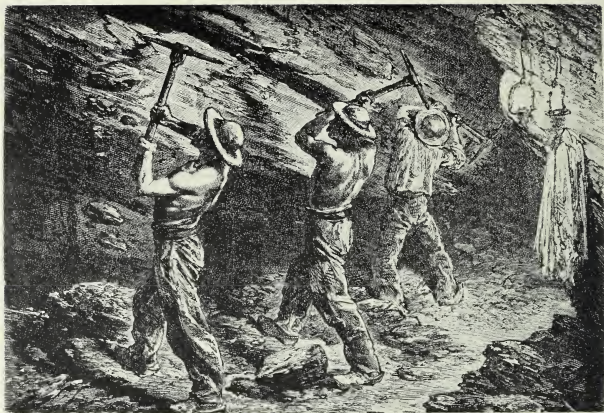
GEMS.



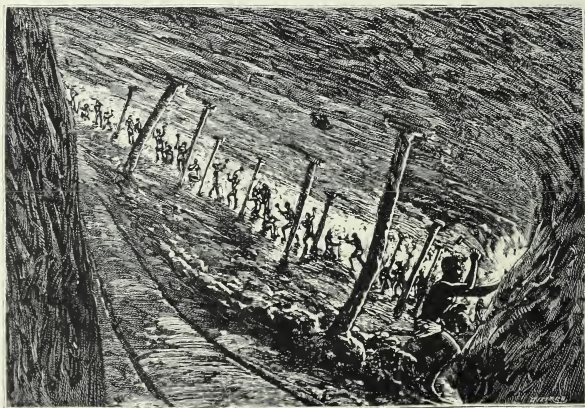


VEINS, FREIBERG, SAXONY.

ONE-FIFTIETH NATURAL SIZE.



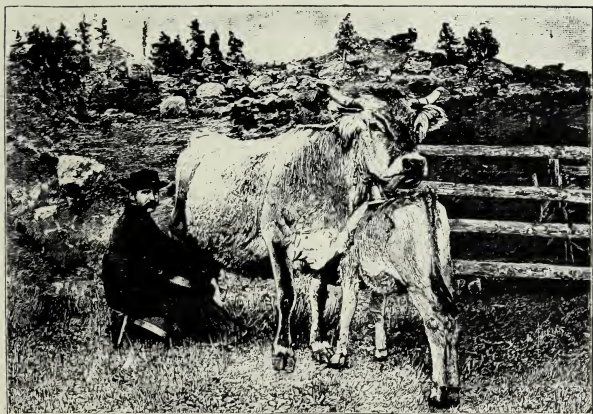
COAL MINING, FRANCE.  
EPINAC.



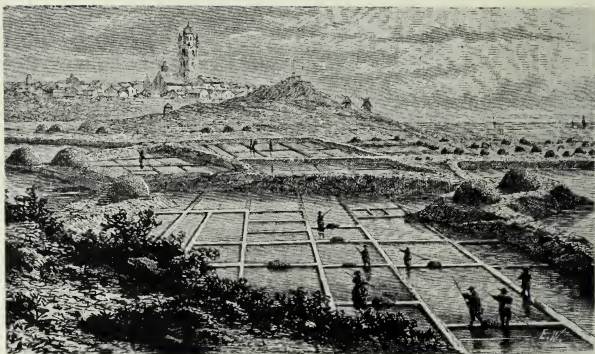
GOLD MINING, TRANSVAAL.  
ZULU MINERS.



VANILLA.  
JARDIN DES PLANTES, PARIS.

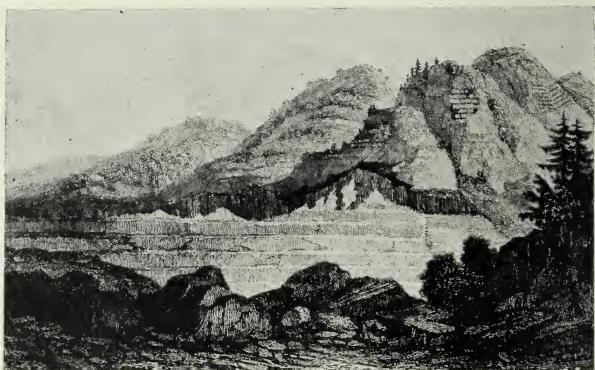


MILK.  
CENTRAL PLATEAU, FRANCE.



SEA SALT, FRANCE.

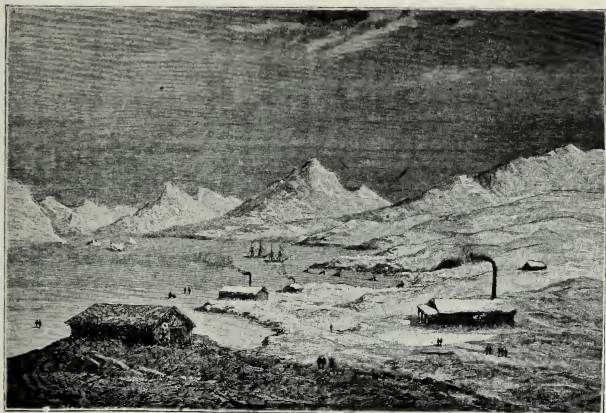
BOURG DE BATZ, BRITTANY.



ROCK SALT QUARRY, SPAIN.

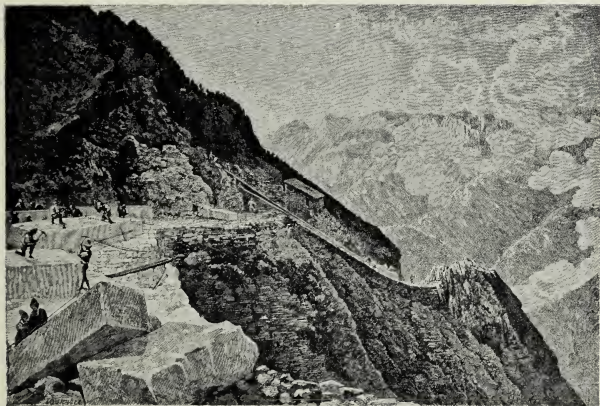
CORDONNA VALLEY, PYRENEES.





CRYOLITE, GREENLAND.

ARKSUT FJORD.



MARBLE, ITALY.

MONTE ALTISSIMO.



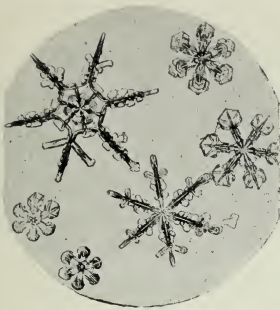
CINCHONA, PERU.

BARK GATHERING.



MAGNETITE QUARRIES, ELBA.

CAPE CALAMITA.



MICROPHOTOGRAPHS OF SNOW STARS.

---

# THE STUDENT'S ATLAS.

## III. THE CRYSTAL WORLD.

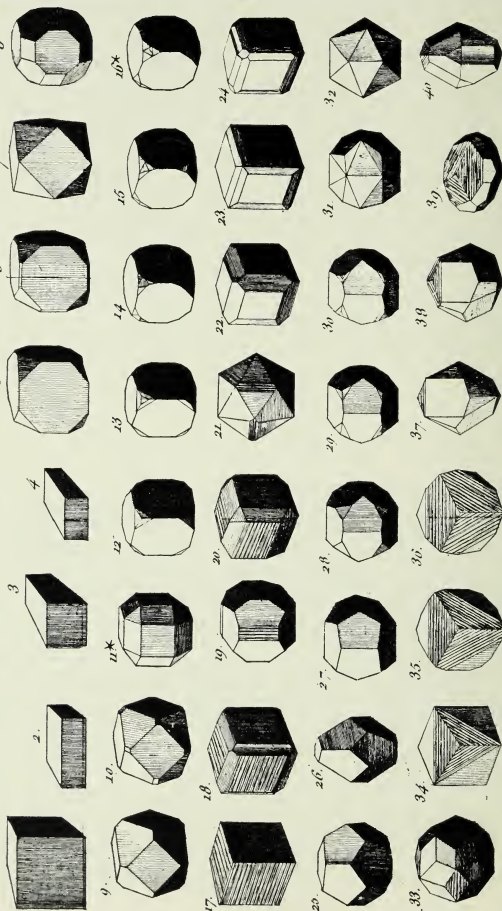


ALEXANDRITE CRYSTALS, SIBERIA.

*Le CUBE ou HEXAÈDRE et ses Modifications.*

Pl. II.

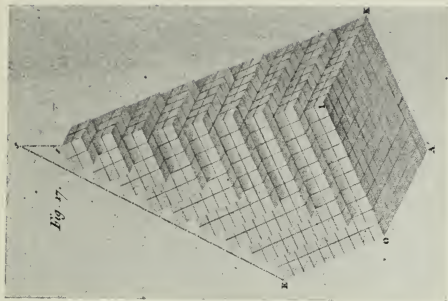
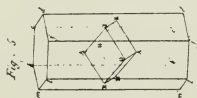
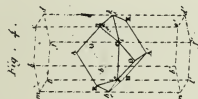
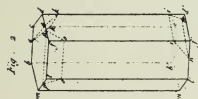
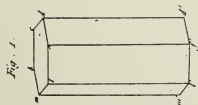
Fig. 1.



ROMÉ DE L'ISLE.

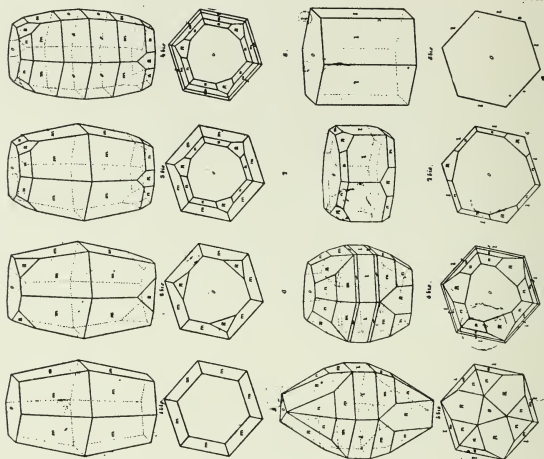
*Desfondaines del et Sculp.*





RENÉ-JUST HAÛY.

## KORUND

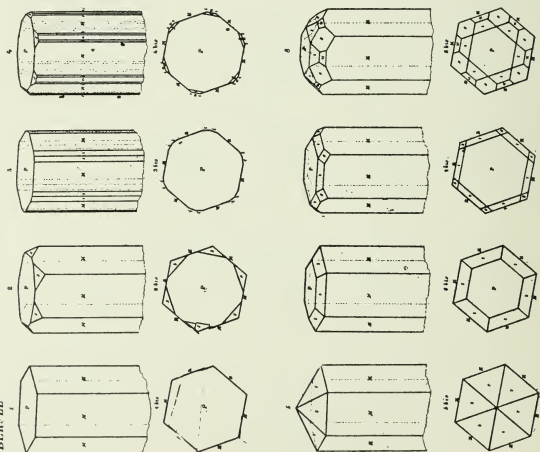


Lith. v. Kroy

CORUNDUM.

## TAF. VII

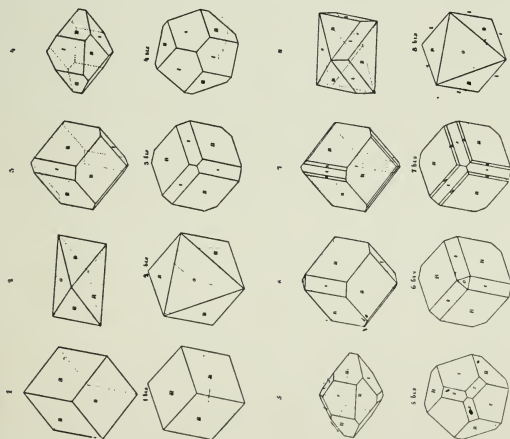
## BERYLL



BERYLL.

TAF I

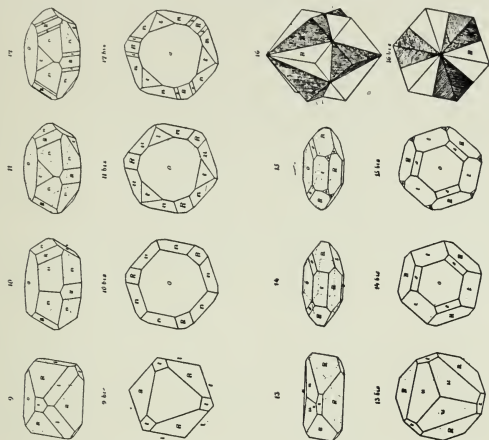
EISENGLAZ



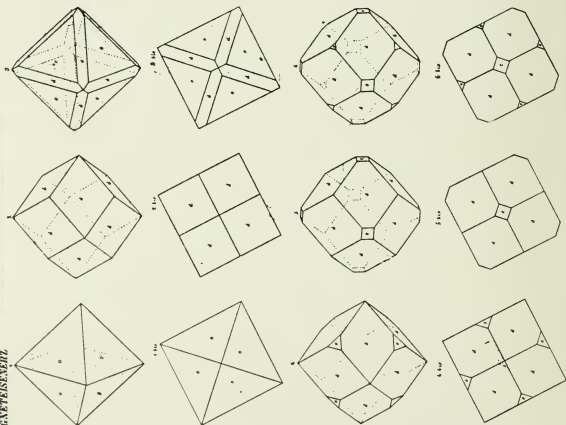
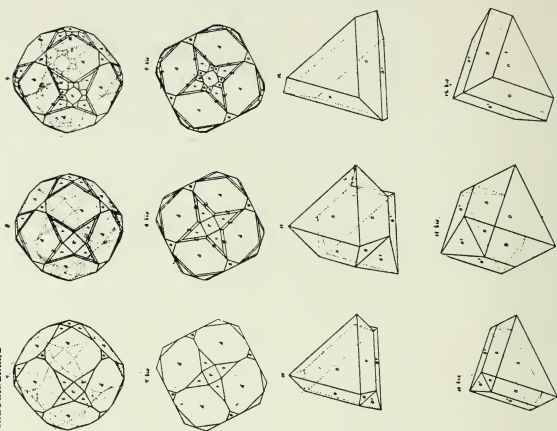
HEMATITE.

TAF II

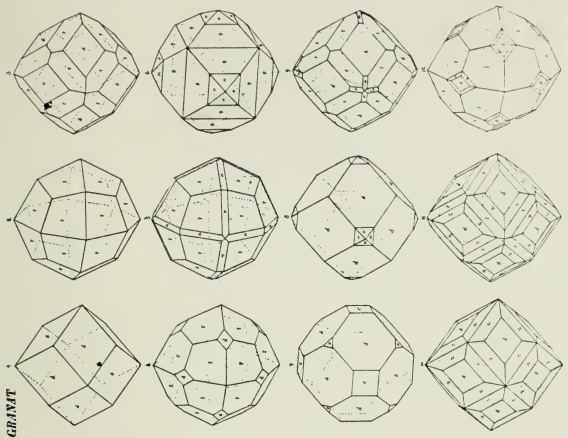
EISENGLAZ



HEMATITE.

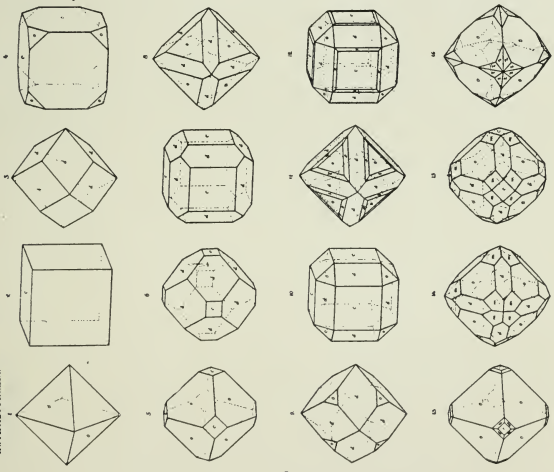


GRANAT



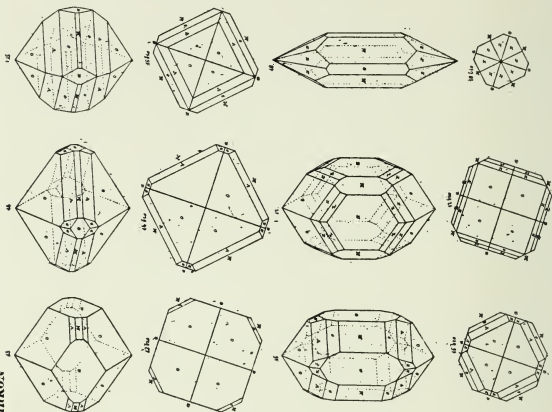
GARNET.

ROTHKUPFERERZ



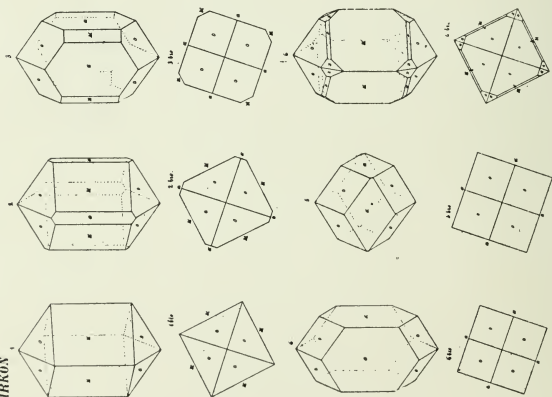
CUPRITE.

ZIRKON



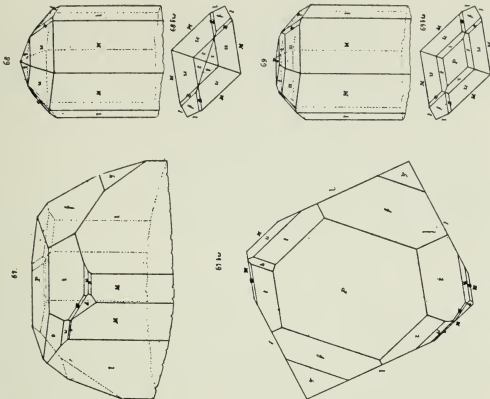
ZIRKON.

ZIRKON



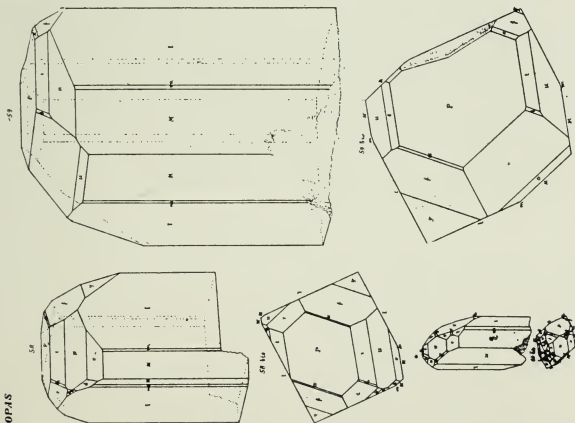
ZIRKON.

TOPAS



TOPAZ.

TOPAS



TOPAZ.

## ALEXANDRIT

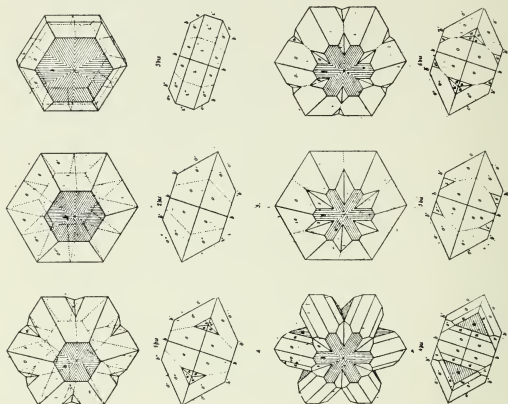
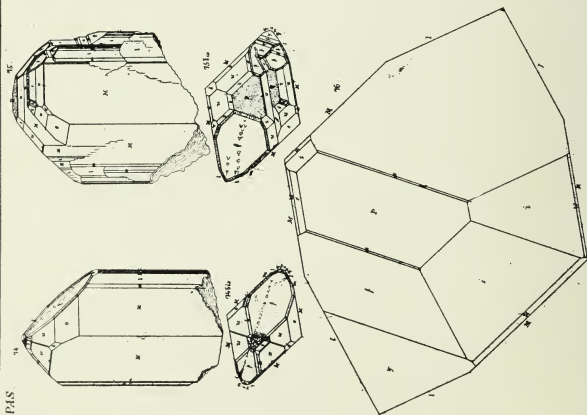


Fig. 1. 2. 3.

## ALEXANDRITE.

## TAF. XXXVIII (F)

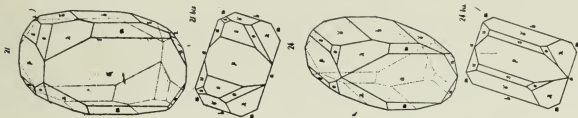
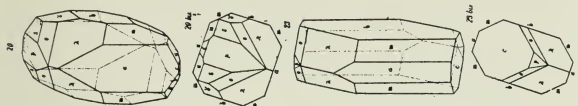
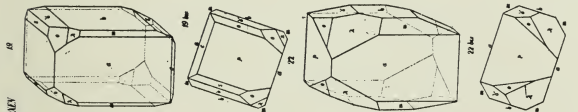


## TOPAZ.

## TOPAZ.

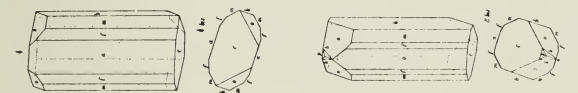
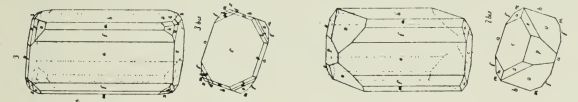


PYROXENE

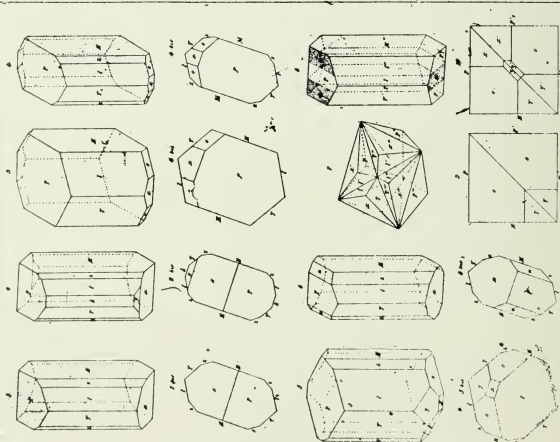


Pyroxene.  
Lith. J. Mader.

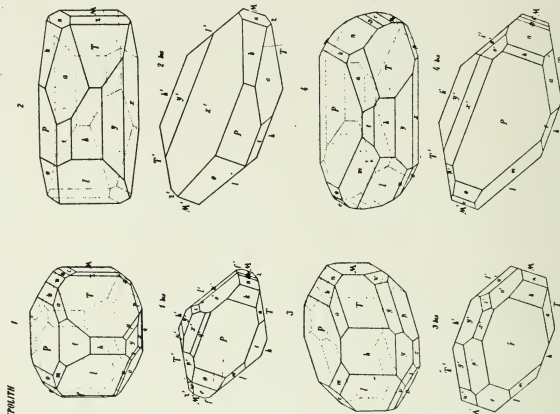
PYROXENE



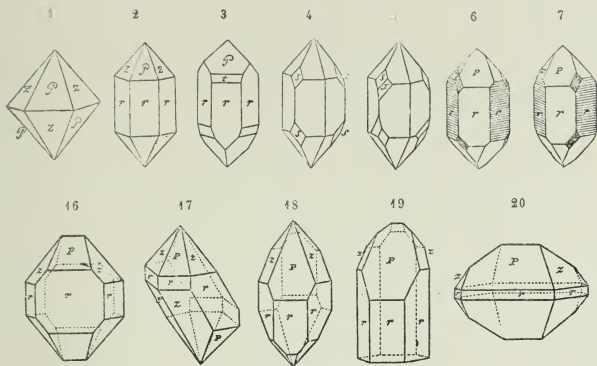
Pyroxene.  
Lith. J. Mader.



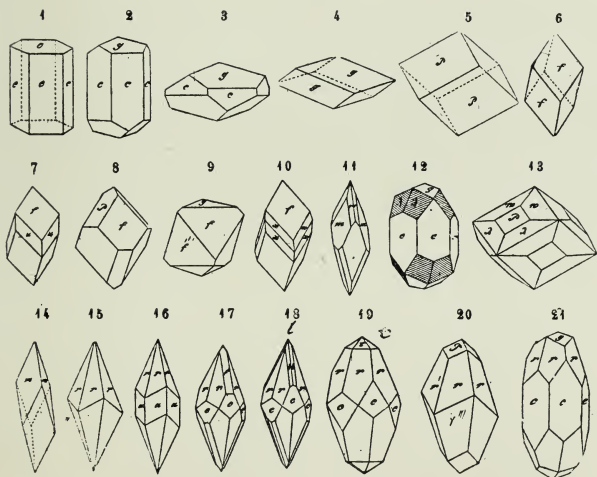
ORTHOCLASE.



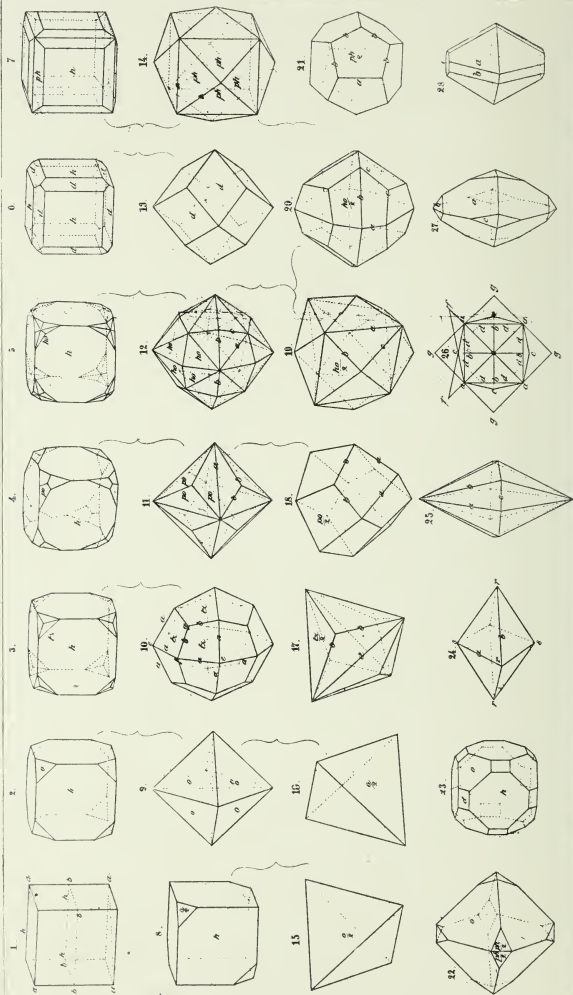
ANORTHITE.

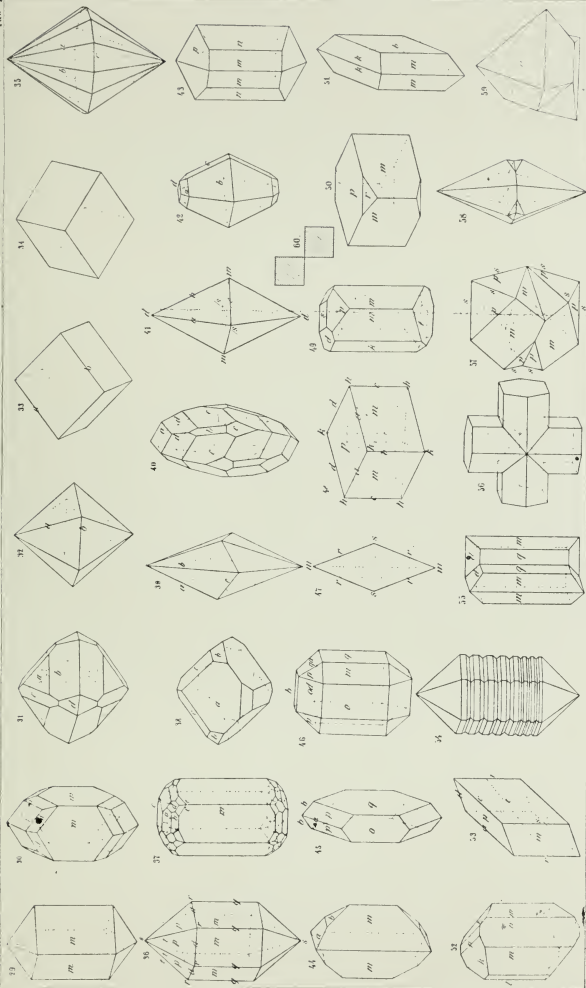


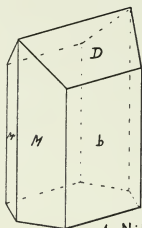
QUARTZ CRYSTALS.



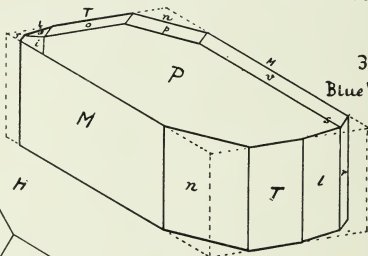
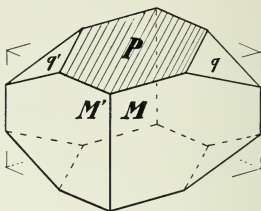
CALCITE CRYSTALS.



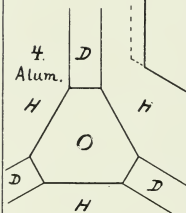




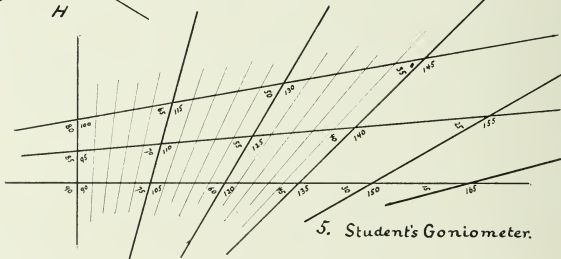
1. Niter.



3. Blue Vitriol.

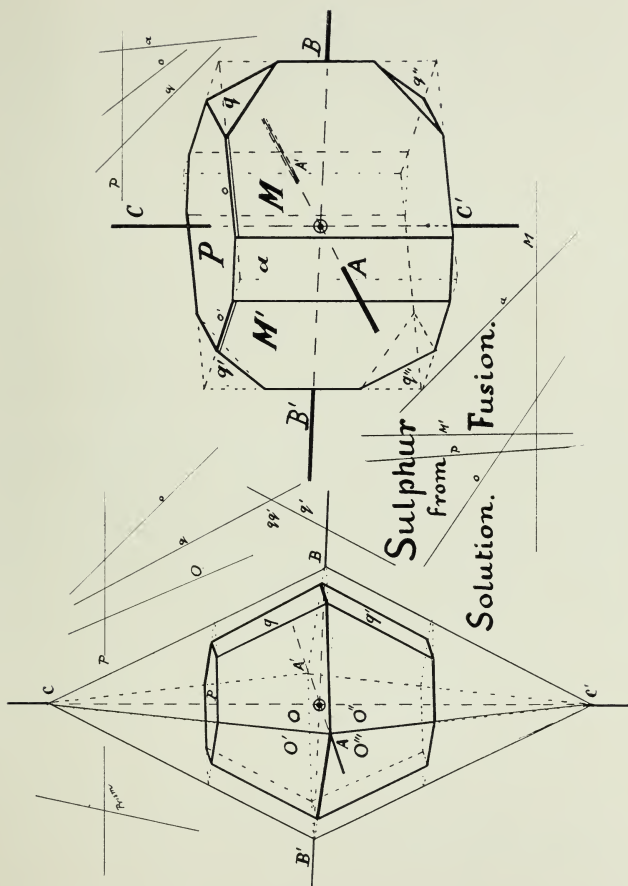


4. Alum.



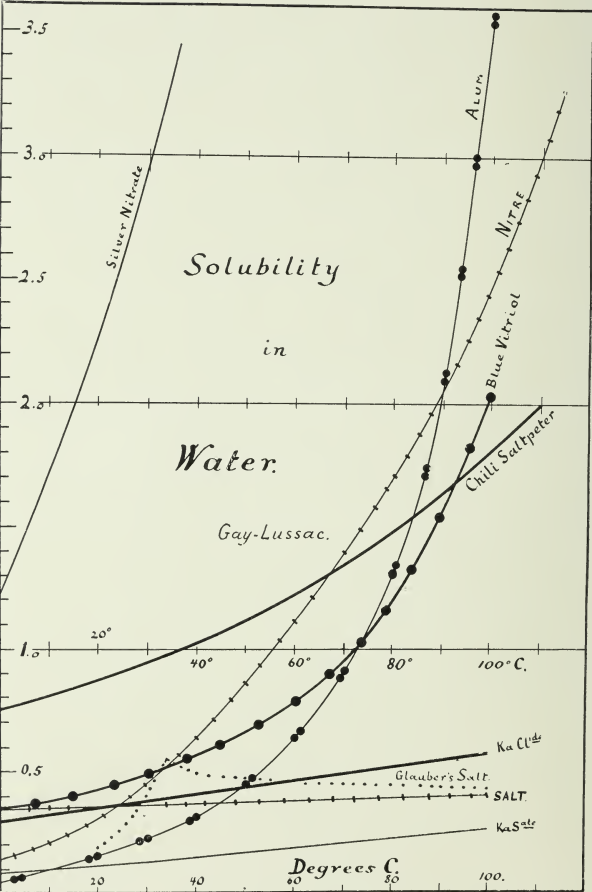
5. Student's Goniometer.

## CRYSTAL DESCRIPTION.

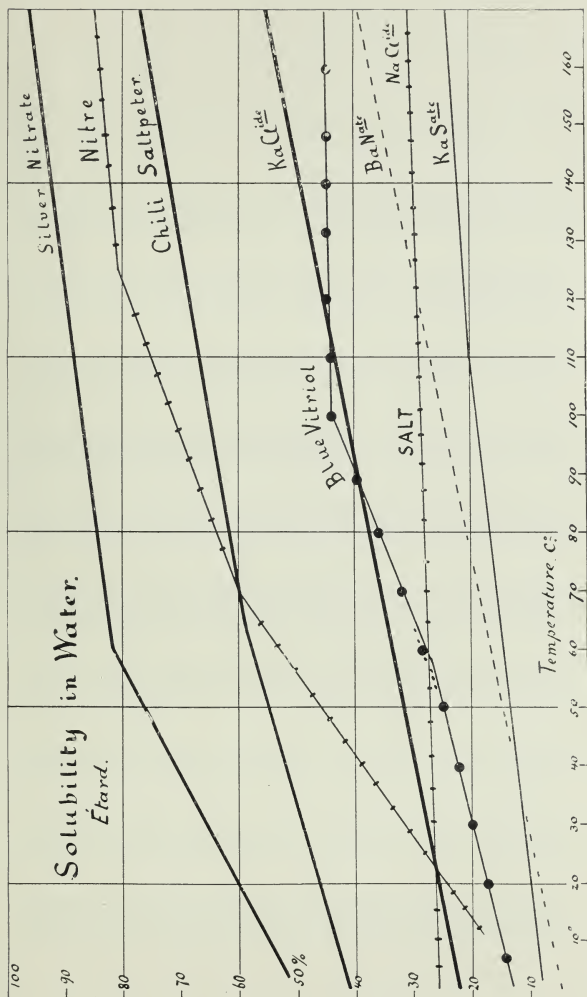


# THE STUDENT'S ATLAS.

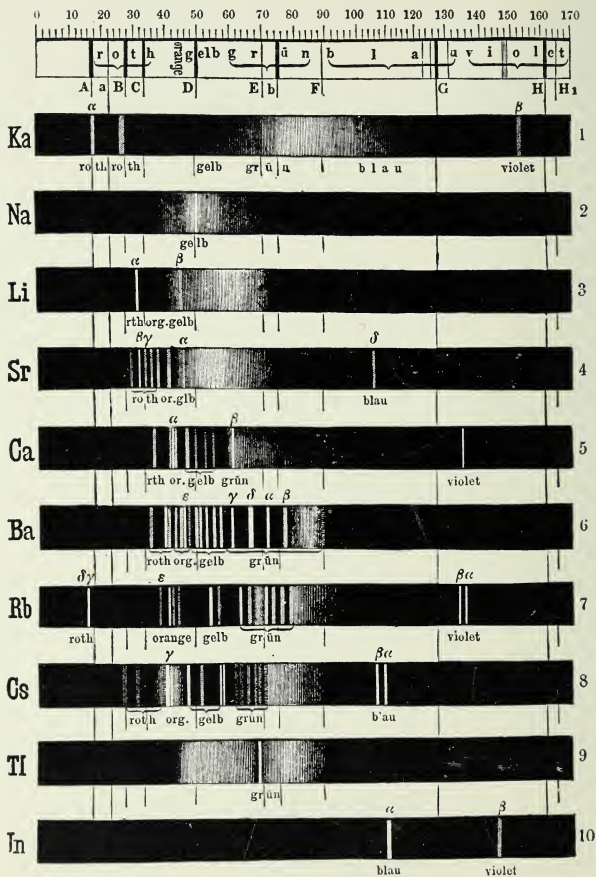
## IV. DIAGRAMS.





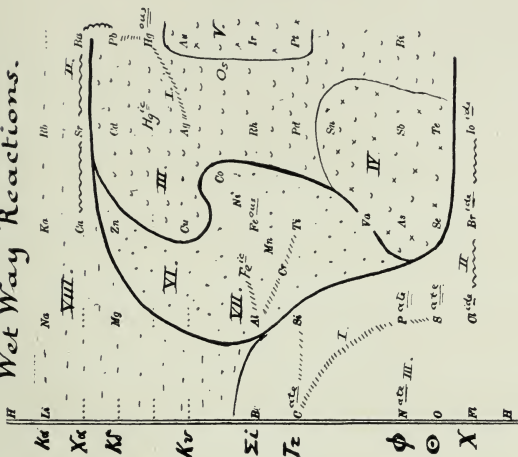


# SPECTRA OF THE LIGHT METALS.



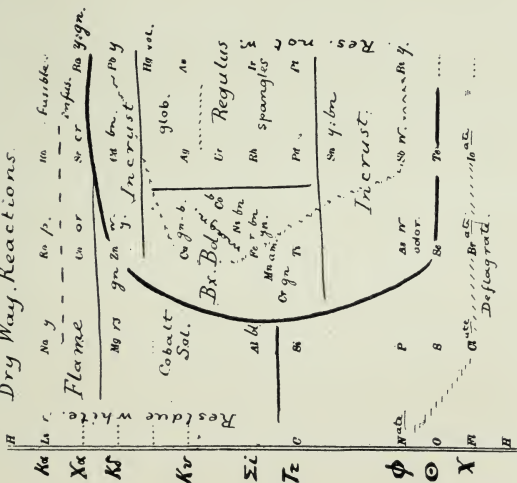
Spectraltafel nach Kirchhoff und Bunsen.

### Wet Way Reactions.

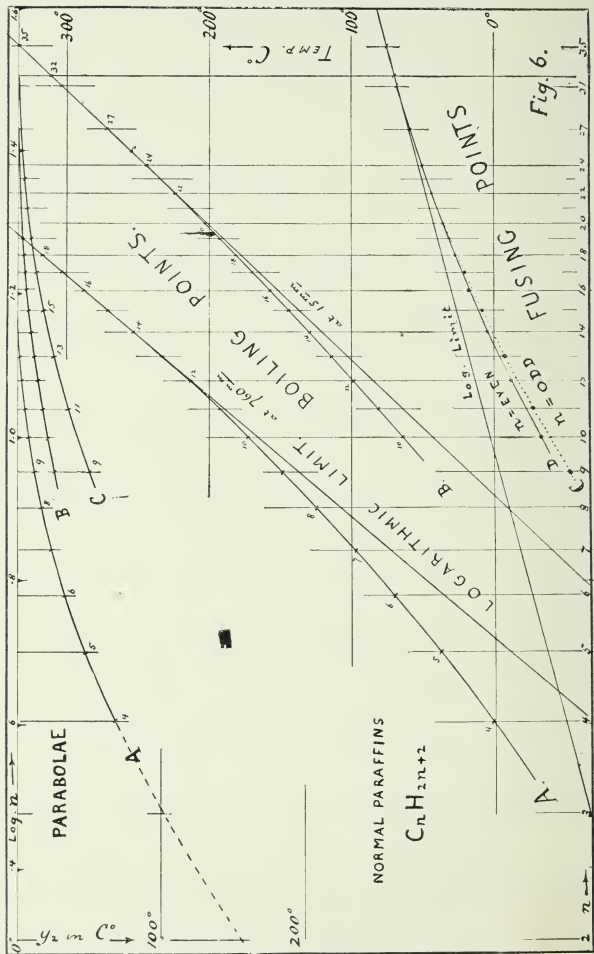


WET WAY.

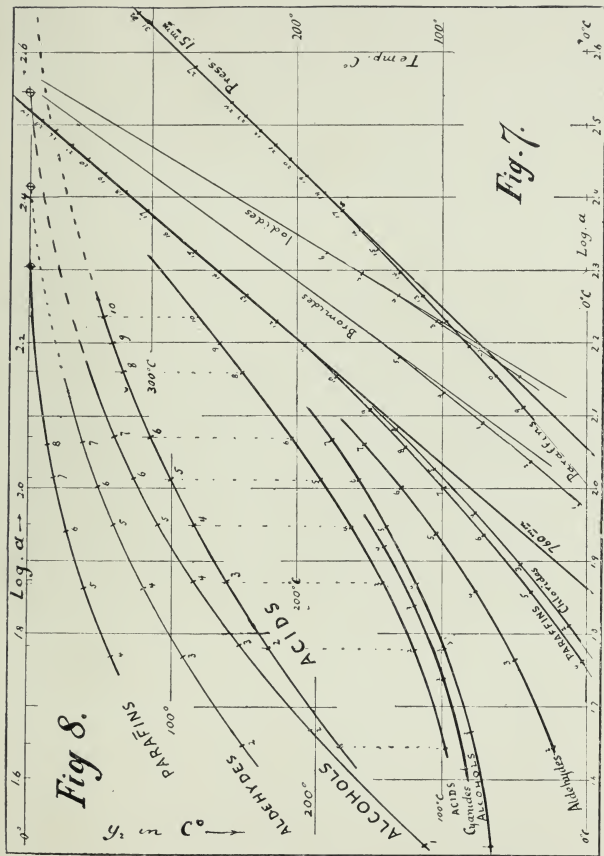
### Dry Way. Reactions.



DRY WAY.



BOILING AND FUSING POINTS OF PARAFFINS.



**Fig. 7.**

BOILING POINTS OF ACIDS, ALCOHOLS, ETC.

# Substitution terminale complexe,

-200° (à Radical)

2  $n$  3

Phénols

Acides

Cyanides

Alcools

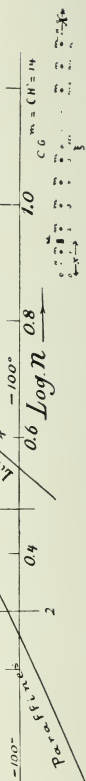
Aldéhydes

$$\Delta t^{\circ} = \frac{K^{\circ}}{n} \cdot \sum \mu v^2$$

$$\mu = \frac{M u}{M + u} \quad v = \frac{\xi - x}{n}$$

$$M = C^{\alpha} H^{10+2} = 2[7n \cdot \xi]$$

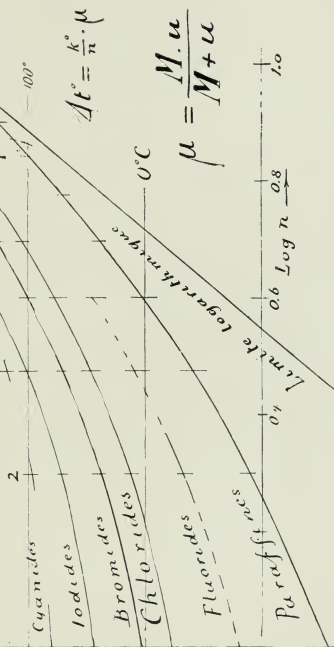
$\xi$ : Centre de gravité de M  
u, x masses et distances  
des atomes additionnels



TERMINAL SUBSTITUTION, COMPLEX.

# Substitution terminale simple,

(à Élément)

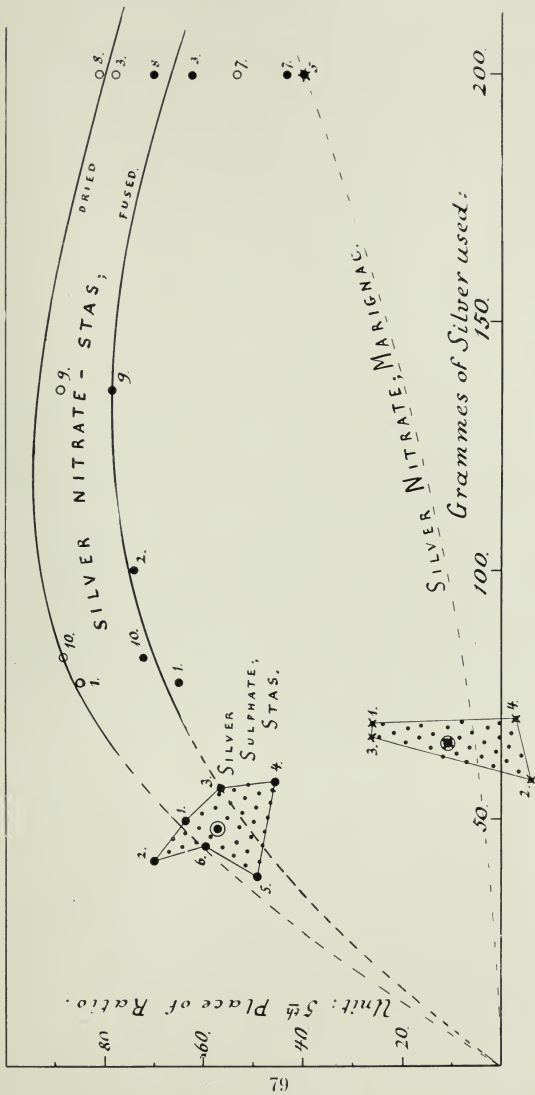


TERMINAL SUBSTITUTION, SIMPLE.

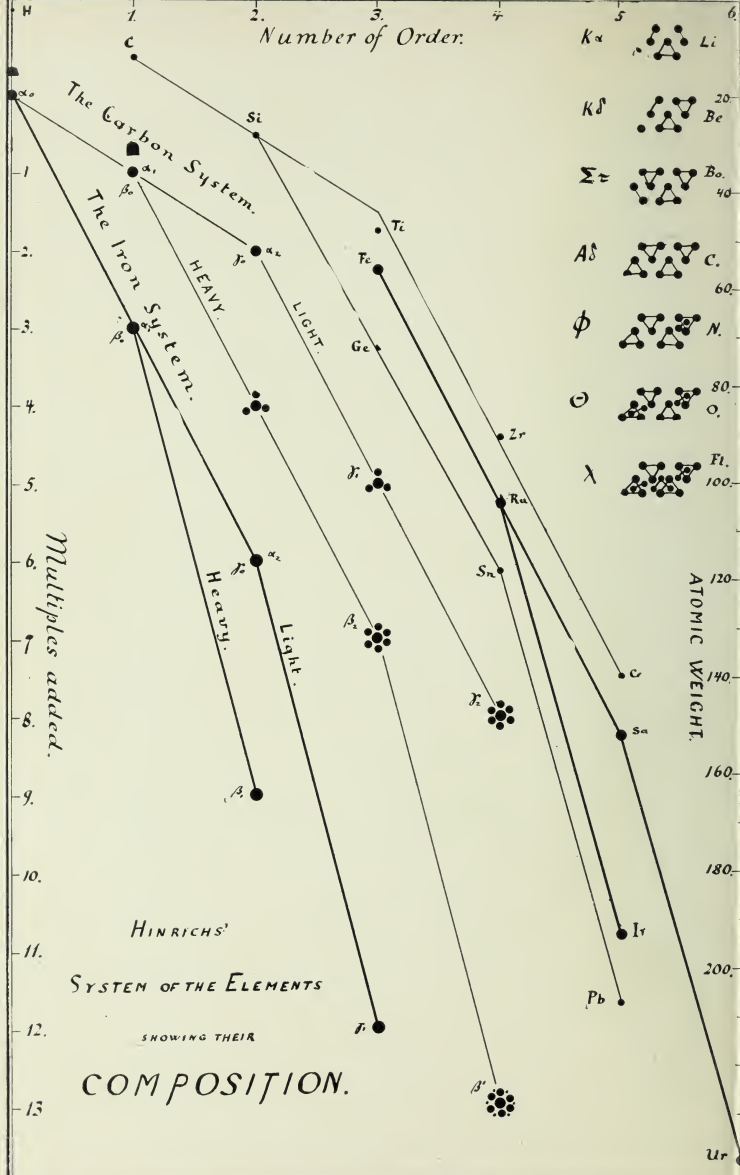




O 2.



STAS' DETERMINATION OF SILVER NITRATE.



## 1. CHEMISTRY AND AL KEMI.

1. CHEMISTRY treats of the changes of matter. It was first practiced by the inhabitants of Kem or Kemi (Egypt). The very name of our science thus proclaims its ancient origin. Atlas, p. 17.

To understand this definition fully implies to have studied the SCIENCE and practiced the ART of Chemistry. Here it must therefore suffice to explain the words used in the definition.

2. MATTER is that which constitutes all things. We all know some metals, stones and ores, representing the inanimate kingdom of nature. Flowers and fruits are vegetable, milk, blood, meat and bone are animal things. Chemistry deals with the changes of matter from all three kingdoms of nature. Nor is Chemistry restricted to materials of this earth; the material of the sun and the stars has been successfully investigated during the last forty years.

3. Motion and division of matter are called PHYSICAL processes; they do not affect the nature of the material itself. The power to produce such motion or division may be great, as witnessed on our railways and in our mills. The immense ball, thrown several miles from the modern cannon, does not change its material nature in this act of motion; however, the charge of powder has disappeared, it has undergone a chemical change.

4. But if that ball be left exposed to the air, the water or the earth, it will gradually be changed into a brownish, non-coherent mass, which we call rust. Smaller and thinner iron things are quite rapidly changed to rust throughout. Objects of copper turn green under like conditions. Gold remains unchanged. The change of limestone to lime in the kiln is also a radical one, practiced from time immemorial to make mortar. Such are chemical CHANGES of matter.

5. Organic matter, that is vegetable and animal substance, chars when heated while the air is partly excluded. Inflammable materials pass off during this process. A specially offensive odor is noted when animal matters are charred. Thus it is generally easy to distinguish mineral, vegetable and animal materials by a simple CHEMICAL TEST.

6. All nature is one boundless CHEMICAL LABORATORY, and the most skillful of all chemists are the plants and animals. From the same soil, water and air, and by the power of the same sunbeam, PLANTS produce not only their diverse materials such as wood, leaf, flower and fruit in general, but each kind of plant produces some more valuable chemical specialty, such as the fragrance of the rose, differing from that of the lily; the potency of the poppy, differing from that of the conium. Atlas, p. 49.

7. In a like manner, every animal is a most wonderful CHEMICAL FACTORY. The beginner should be impressed with such primary fact as the chemical change of grass and water into milk. Surely, grass, water and air are the only raw materials accessible to the cow in her pasture. And what a remarkable chemical product is the milk produced, containing butter, cheese, sugar, and mineral salts dissolved and suspended in water! Atlas, p. 49.

8. Seeing the INFINITE DIVERSITY of organic matter produced from the identical simple raw materials of soil, water and air, we can understand that profound thinkers, twenty five centuries ago, considered all matter essentially one in kind. For about a century this idea has been generally derided by chemists. It does not seem to us that the ancient sages were greatly in error.

9. But if all matter be essentially one, it seems possible that any material might be made by art if only sufficient knowledge had been acquired. Hence ancient chemists (ALCHEMISTS) endeavored to make gold from common metals, and tried to produce an elixir to give health and prolong life.

Working to realize these high ideals, they laid the foundations of CHEMICAL ART AND SCIENCE, the two equally important parts of CHEMISTRY. The science we present in the lecture hall, the art we practice in the laboratory. Atlas pp. 40, 41.

10. Chemical science has ever enabled chemical art indirectly to make gold, and thus to REALIZE THE IDEAL OF THE ALCHEMIST. Clay was converted into costly porcelain; coal tar was changed into the colors of the rainbow, and apparently worthless ores are now yielding gold by the million dollars in Transvaal and in Colorado. Atlas, p. 48.

11. Chemistry is also approaching the second ideal of its founders. The active remedial principles have been extracted from many plants, and even new remedies have been produced by direct synthesis, the chemist imitating the work done by the living cell! Moreover, practical hygiene is mainly chemical. Surely, Chemistry does give health and prolong life.

12. Until it shall be deemed proper to deride Columbus for having discovered America while he sought the Indies, we will not join those who deride the early workers in Kemi for having held ideals too high to be fully realized in three thousand years. In Chemistry, as everywhere else, the highest ideals are the best; the distant star is a better guide than the near ignis fatuus. Sic itur ad astra.

---

NOTES. Deeming it essential to keep the text as brief and clear as possible, collateral and explanatory matter, aiding in the understanding of the topic presented, is appended in the form of short notes, precisely as explanations are given at the lectures, but not considered as part of the subject itself, once that being understood. The notes will be prefaced by a numeral referring to the paragraph for which they are intended.

1. Chemistry, in English, is commonly pronounced Kem-istry; signifying knowledge pertaining to Kemi. Chemistry is called Kemi in Danish, Chemie in German and Chimie in French.

6. Among the various plants represented in the cut as growing in a glass-house of the Jardin des Plantes at Paris, the climbing Vanilla will

be noticed, showing flower and the valued FRUIT, also numerous pendent air roots.

7. These Chemical factories (cows) are exceedingly numerous and their product aggregates millions a year in every country. When no longer wanted for milk production, these factories are let alone, and produce meats and fats, hides and bones, all prime materials of the highest importance. England imports for 40 million dollars butter alone a year.

10. The new cyanide process with reduction by electrolysis makes it possible to work low grade ores profitably. The Zulus do the mechanical work of drilling, shown p. 48; dynamite does the rest. The Transvaal gold deposit is not a vein, but a stratum, the only stratified gold deposit in the world.

## 2. WEIGHT AND MEASURE.

1. Any body or thing occupies some definite amount of space, called its bulk, measure or VOLUME. It also exerts some definite amount of pressure upon its support; this pressure is called its WEIGHT. Weight and measure are the only two general properties which matter possesses.

2. By adopting convenient UNITS, both weight and volume can be expressed by numbers. The standard units are the KILOGRAMME and the METER. Exact copies thereof are made at the International Bureau of Weights and Measures, in the Pavillon Breteuil at Saint-Cloud, in southwestern Paris. This Bureau is jointly maintained by over twenty countries, including the United States and Great Britain. Atlas, p. 39, shows the Balance Hall of this Bureau.

3. The metrical standards were adopted in France a century ago, to secure natural units and uniformity; even towns having distinct units at that time. The meter was intended to be the ten-millionth part of the earth's quadrant passing through Paris. The kilogramme was intended to be the pressure of a tenth-meter cube of water at its greatest density.

4. Modern determinations have shown that the quadrant really is about 10.001.900 meters and that the kilogramme exceeds the defined amount by something less than one ten-

thousandth part. The actual material STANDARDS, made a century ago are, however, retained unchanged by the International Commission; the original definition being sufficiently complied with for practical purposes.

5. The system of numeration in universal use being DECIMAL, the units of weight and measure must also be divided and multiplied by tens to avoid useless reductions. The sub-multiples are distinguished by Latin prefixes (deci, centi, milli), while the multiples are designated by greek prefixes (deka, hecto, kilo). The mega is used for very large (million) and the micro for equally small (millionth) values. Thus the micrometer or micron ( $\mu$ ) being the thousandth of a millimeter, is the usual unit for microscopic objects.

6. THE BALANCE is the instrument for weighing. It consists of a light, rigid beam, resting by means of a transverse edge on a hard smooth plane. Two smaller edges at the ends of the beam support like planes to which the pans are attached. The distances from the outer to the central edge (the arms) must be equal.

In good (prescription) balances, edges and planes are of hardened steel; in the analytical balance, the planes are of agate; in the best balances, the edges are also made of agate.

7. WEIGHTS are made in sets, containing one 5, one 2 and two 1 for each digit, except the last, for which commonly two 2 and one 1 are given to complete the 10 and allow a check. From one gramme up, the weights are usually turned brass; for subdivisions of the gramme, platinum foil is used. Each single weight is fitted to its special place in the box holding the set. Chemical weights must be handled by forceps only, never touched with the fingers.

8. In WEIGHING, the body is placed on the left pan, and weights are applied in the order of their magnitude on the right pan. By a simple mechanism, the beam is brought into action only for an instant to see whether the weights on the pan are too heavy or insufficient. Below the centigramme,



the beam is permitted to oscillate, the balance case being closed to prevent air currents. If the oscillations of the pointer are equal on both sides, the weighing is completed.

9. Balances and weights obtained from reputable makers will stand all TESTS warranted by the price paid. All details about these matters belong to the course in practical chemistry.

The balance being the most sensitive and accurate instrument of all, the chemist checks his volume measures by weighing them empty and filled with water up to mark. Every cubic centimeter (cc) should correspond to a gramme (gr.)

10. For the ready measurement of volumes the chemist uses sets of glass vessels accurately graduated (BURETTES and CYLINDERS) or provided with a mark filled up to which they hold a definite amount (FLASKS and PIPETTES). Graduated cylinders with ground glass stoppers are also called MIXING JARS. The burettes are either provided with a rubber tube and spring clamp (Mohr's), or with a perforated ground glass stopper (Geissler's) for use with corrosive liquids.

11. Common experience shows that bodies differ greatly in density; lead is heavy, chalk is light, cork even lighter than water.

The SPECIFIC GRAVITY (G) of a substance is the weight, in grammes, of one cubic centimeter thereof. The specific gravity, carefully determined, is an important characteristic of matter, enabling us to distinguish otherwise similar bodies. Thus one cc of lead weighs 11.35 gr.; or lead is characterized by its G being 11.35.

12. To determine the specific gravity of any body, ascertain its weight (w) in grammes and measure its volume (v) in cubic centimeters; dividing the volume into the weight, we evidently obtain the weight of one cubic centimeter, that is the value of G. This process applies to all bodies; the special methods of measuring vary with the nature of the body. A ten gramme flask holds 7.94 gr. of absolute alcohol; hence G is 0.794 for this liquid.

### 3. SOLIDS AND FLUIDS.

1. Matter presents itself in three distinct forms, namely as solid, liquid and gas. These forms are also called the three STATES OF AGGREGATION. Ice, wood, iron, copper, are solids; water, oil, alcohol, are liquids. The most common gas is atmospheric air.

2. Hold any SOLID body in varying positions, especially in reference to the vertical, and no change in either shape (form) or bulk (volume) of the solid will be noticed. That is, solid bodies possess a form and volume of their own. In other words, the volume and form of a solid are fixed (constant) quantities.

3. A LIQUID contained in any glass vessel, handled in the same way, will exhibit in all positions a free surface which is plain and level, otherwise it will conform to the shape of the containing vessel. If the volume of the liquid is measured at the beginning and at the close of such experiment, it will be found to have remained unchanged. Thus liquids have a fixed volume, but no form of their own.

4. The FREE SURFACE of the liquid shows near the walls of the containing vessel a curved surface; concave for water, convex for mercury in glass vessels. If a tube be inserted, the liquid will rise or sink so much the more as the tube is more narrow or hair like (capillary). Hence the cause of this deviation from the plane surface is called CAPILLARITY.

5. Only vessels sufficiently wide will show the true plane and level free surface of the liquid. To FILL TO MARK or read the volume on a graduation, the eye should be brought exactly in the height of this surface. If the vessel be too narrow, the lower (for mercury the upper) curved surface should be tangent to the mark of capacity or graduation.

6. The free surface of the same liquid contained in two VESSELS, COMMUNICATING by means of a sufficiently wide tube, stand always in the same level, however the position of

the vessels may be changed. This is readily seen by using the burette with reservoir, or our gas burette open, and with any liquid, including mercury.

7. If the exit tube of the gas burette be closed, the free surface of the liquid in the burette and reservoir will no longer be in the same level; it will stand low in the burette if the reservoir is raised, and vice versa. Consequently the AIR in the burette resists the pressure of the liquid in the reservoir, and expands when the reservoir is lowered; it is a substance or body.

8. Thus the air in the closed gas burette has neither volume nor form of its own; its form is that of the containing vessel, and its volume is dependent on the pressure to which it is subjected. Such a body is called a GAS.

Liquids and gases flowing freely from one vessel to another, are also designated by one term FLUID. A liquid is a fluid of fixed volume; a gas is a fluid of variable volume.

9. A gas may be handled almost as readily as a liquid, by means of the pneumatic trough, flasks and cylinders. The PNEUMATIC TROUGH is simply a wide vessel containing a liquid (water, mercury) in which cylinders, flasks, etc., can be filled with the liquid and inverted; they will remain filled, and receive and retain gas from any other vessel or delivery tube. A few experiments make this familiar. See also plate of gas apparatus.

10. A gas burette filled with mercury and provided with a stop-cock at the top can be used as BAROMETER and as a mercurial air pump.

By raising the reservoir, fill the burette to a little above the stop-cock, then shut this. Now lower the reservoir. The burette will remain filled with mercury so long as the surface of the mercury is not more than 76 cm lower than the stop-cock. If lowered more, the VACUUM will appear in the burette, and the column of mercury will remain invariably 76 cm. This corresponds to Torricelli's experiment (1642).

11. To use the burette as mercury AIR PUMP, its stop-cock must be perforated lengthwise and connected with the receiver to be exhausted. By a simple turn of the stop-cock, the burette can now be closed (A), or communicate with the air (B) or with the receiver (C). In position (B), fill the burette with mercury, by raising the reservoir; then close (A) and lower reservoir 76 cm; now connect with receiver (C); then turn to B, raise reservoir and drive out air. Continue these operations, and the air in the receiver will rapidly be reduced in amount.

12. If the burette be equal to the capacity of the receiver, the amount of air withdrawn at each complete motion is one half, leakages neglected. Ten motions would reduce it to the thousandth part of the original.

If a U tube with perforated stoppers and a capacity of from 50 to 100 cc be exhausted, it will show a loss in weight of over one milligram per cubic centimeter. This evidently is (approximately) the WEIGHT OF THE AIR.

---

NOTES 3. Before filling the vessel, FILM it, that is, move a small amount of the liquid around in the vessel so as to cover the inside with a film of that liquid; then let run and drip out all that will flow. If the vessel was not filmed, the volume of the liquid used in the experiment would apparently have diminished slightly.

## 4. FUSING AND BOILING.

1. Solid ICE brought into a warm room melts or fuses, being converted into liquid WATER. The latter, heated in a flask, soon begins to boil; while condensed vapor (liquid drops) issue at the top, the flask above the water looks as if it contained air, that is the true STEAM, water in the gaseous state.

Solid IODINE is also readily melted and converted into beautiful violet vapor. The corresponding experiment with SULPHUR requires care, the vapors burning with explosive violence.

2. In general, a fusible solid, upon heating, will melt, and a volatile liquid will boil. By decreasing the heat, the vapor will again liquefy (condense), and the liquid will solidify (frequently crystallize). Thus the state of aggregation of a substance depends not only on the nature of that substance, but essentially also on the temperature to which the substance is exposed.

3. Heat does not change gases, except in bulk. Grasp the receiver of our gas burette firmly with the hand, and the motion of the liquid will show that the air EXPANDED. Withdrawing the hand, the air returns to exactly its original volume. This apparatus accordingly is a sensitive AIR THERMOMETER. With porcelain and platinum receivers, it permits the determination of very high and also very low degrees of heat. Common thermometers contain mercury or alcohol.

4. Inserting the bulb of such a thermometer into crushed ice, the thermometer will first fall rapidly, then more gradually, and finally remain perfectly stationary or fixed, so long as a reasonably large amount of ice remains. This FIXED POINT of temperature at which ice melts is called the freezing point, and marked zero. In the same manner, boiling of water is found to take place at a fixed point, called the boiling point, which is marked 100.

5. The interval (volume in burette or in thermometer tube) is divided into 100 equal parts, called DEGREES of temperature. For air thermometers this division is continued indefinitely upwards and downwards.

6. If the reservoir be a 100 cc pipette melted off at the mark, and connected by narrow tube with (mercury) gas burette, and the reading of the burette be taken while the reservoir (bulb) is packed in melting ice and also when surrounded by steam of boiling water, the EXPANSION will be found equal to 36 cc. Accordingly it is 0.36 cc per degree for 100 cc. Gay-Lussac.

7. In the same manner, the FUSING POINT (F) of any solid is that fixed degree of temperature at which the solid changes to a liquid; so long as any notable amount of solid is left, the thermometer will remain stationary. If the crucible with the molten mass is set aside to cool, the crust broken and the remaining liquid poured out, the wall will often be found studded with beautiful crystals. Examples: Sulphur; Bismuth.

8. When heating a volatile liquid in a flask provided with a thermometer, the temperature will first rapidly rise, then gradually become stationary, when the liquid will begin to boil, forming bubbles of gas throughout its mass. This fixed temperature is the BOILING POINT (B) of the liquid. When the vapors of the liquid are inflammable, the flask must be connected with a condenser. EVAPORATION is the formation of vapor at the surface of the liquid only.

9. A CONDENSER consists of an inner tube through which the vapors pass from the bulb or flask to the receiver, surrounded by an outer tube through which a current of cold water is kept flowing in the opposite direction of the flow of the vapors. Accordingly, the chance of their condensation increases as they pass on. The Liebig condenser is the most common form in use. Atlas, p. 23.

10. This entire process, comprising the change of liquid into vapor, followed by the condensation of the vapor to a liquid, is called DISTILLATION. All non-volatile matters will remain in the flask; hence distillation enables the chemist to separate the volatile from the non-volatile matters.

If the vapors condense to a solid, the operation is called SUBLIMATION. Example: Iodine.

If the thermometer remains stationary, it marks the boiling point (B) of the pure liquid. If the thermometer is not stationary, the substance is a mixture.

11. In such cases, the process of FRACTIONAL DISTILLATION will separate these different substances and yield nearly



pure materials. The portions or fractions of the distillate, passing over between definite degrees of temperature, are kept separately; these fractions are again run through the distilling apparatus in succession, always removing the new fractions when the same limits of temperature are obtained. After four or more such runs, the fractions often pass over without change in temperature, and thus represent single substances.

12. These two fixed points F and B are most CHARACTERISTIC numbers for a given substance, often readily distinguishing otherwise closely resembling materials; hence they form, together with G, the most important part of the scientific description of a given substance. If the material has no such fixed points, it is thereby proved to be impure, and should be subjected to fractioning, to separate it into its principal ingredients.

## 5. FURNACE AND BLOWPIPE.

1. HEAT not only produces the physical changes of volume and state of aggregation, but it also is one of the common causes of CHEMICAL CHANGES. Inversely, the latter often produce heat. This is especially the case in the general process of COMBUSTION, a chemical action of combustible and air. When either combustible or air is withdrawn, combustion ceases.

2. WOOD is the oldest combustible used; it produces first a flame or blaze, and when the volatile combustible material is burnt, the intensely glowing coals remain. Such a fire is too unsteady for most chemical purposes. Hence, wood first is charred, by slowly burning with limited supply of air, and the resulting CHARCOAL is used. It was the only combustible of the early chemists.

3. In modern days, combustible liquids and gases have come into general use in laboratories. In the days of Berzelius, ALCOHOL was used, especially in the excellent lamp with

double draft, constructed by him. For many years illuminating gas—the volatile part of bituminous coal—has been accessible nearly everywhere; it is the best combustible for most laboratory purposes. Where gas cannot be had, gasoline is frequently used. Atlas, p. 22.

4. An ordinary gas flame is brightly luminous, but not very hot; a cool vessel held over it will be soiled with soot. For heating purposes, a gas flame evidently needs a more abundant supply of air. In the BUNSEN BURNER, this object is perfectly attained, by surrounding the small gas jet with a wide air tube or chimney, open below. Such a burner gives a tall, steady, almost invisible flame, very hot and depositing no soot. Glass tubes are bent and drawn easily in this flame. Atlas, p. 24.

5. The Bunsen Burner is used in all laboratories the world over, singly for ordinary work, grouped into FURNACES for heating larger forms of apparatus, such as tubes and crucibles. These furnaces are provided with fire clay slabs, disks, wide tubes, to support or encase the vessel, so that the heat may be concentrated upon the vessel and not dissipated to the surroundings. Example: The so-called combustion furnace for elementary analysis

6. The highest degree of heat can only be obtained by burning a large amount of gas completely by means of a correspondingly large supply of air. Accordingly, the gas tap must be large, and the air must be forced by a bellows into the center of the flame. Glass is readily fused in such a BLAST FLAME, and platinum crucibles are brought to white heat almost instantly. Forms of blast and blast furnaces are very numerous, many makes being most excellent.



Glassblowers in ancient Egypt.

7. By means of the chemical BLOWPIPE, all the effects of furnaces may be obtained on a small scale; it is truly a

miniature furnace. After a little careful practice, an intensely hot flame may be maintained steadily and on a minute sample produce almost instantly the varied effects of furnaces. The chemical blowpipe was perfected by Swedish chemists of last century and became universal through BERZELIUS. Atlas, p. 22.

8. The main difficulty in using the blowpipe consists in keeping up a steady flame independent of the regular work of the lungs. TO INHALE AND BLOW at the same time seems impossible; but it is quite easily done, if the respiratory outlet be rigidly limited to the nose (which was specially made for that) while the cheeks fully distended, by their elasticity keep up the flow of the small amount of air required for the blowpipe.

9. Where much blowpipe work is to be done, the inner tube of a so-called COMPOUND BLOWPIPE may be connected with foot bellows, while the outer tube is connected with the gas tap. With such an apparatus, blowpipe work may be exhibited to a class during lectures.

10. In every good blowpipe flame THREE REGIONS are distinguished. At the luminous, bluish point the heat is greatest; it is the FUSING POINT (borax beads, flame colorations). Beyond that point is the OUTER FLAME, assisting combustion and producing calcination of metals; within is the INNER FLAME, in which the calx may be reduced again to the metallic state. Example: Lead, supported on charcoal; flame colorations of nitre or salt; borax beads with copper or cobalt calx.

11. As SUPPORT for substances while being heated, glass, porcelain, platinum and carbon, are most generally used for experimental purposes. Fireclay and bone ash are also employed.

The best chemical glass is the so-called Bohemian glass, which is light, hard and difficultly fusible; when heated in a Bunsen flame, it is not quick to color it, and first tinges it purple only. Tubes of such glass are most useful.

12. Porcelain in the form of dishes, crucibles and tubes, will stand a higher heat than glass. Platinum vessels and carbon (charcoal and graphite) are used at the highest temperatures.

For blowpipe work, hard glass tubing, platinum wire and foil, and good charcoal are all that is required. The properties recognized by blowpipe work are commonly called PYRO-GNOSTIC PROPERTIES (Berzelius).

---

NOTE.—In this lecture, as in all others, the objects referred to are abundantly exhibited, and the operations mentioned, are produced before the class. Thus work on glass (especially tubing) and metals is exhibited; flame colorations and beads are shown. The manganese bead is amethyst in the outer, colorless in the inner flame.

## 6. METALS, OLD AND NEW.

1. Two substances have attracted the attention of man in the earliest times, and continue to busy his thoughts to-day. The one is and ever has been most precious to him, so that he is willing to accept a small portion thereof as reward for his labors. The other first was his heaven-sent weapon, has become the tool of his hand and mind; he even endeavors with it to build higher than Babel.

2. GOLD is the one of these bodies. Hardly any rich gold deposit is left in the long inhabited countries, but history and myth show they were once as rich in gold, as California and Australia in the middle of this century. Gold has the brilliant luster (metallic) in a high degree; its color is yellowish; its density almost twenty times that of water; when struck a blow, it yields (is malleable). Fire does not change it; it is rare, it cannot be overlooked or mistaken. It is gold.

3. Primitive man also found another metal (luster, malleable, heavy), in large lumps, grey in color. We have record of early falls from heaven of such masses of malleable IRON

at Aegos Potamos on the Bosphorus. Such METEORITES are represented on ancient medals and coins. In the time of Homer iron was prized with gold. Many large meteoric iron masses have been found in Mexico, near the Texas border; also in Southeast Africa, where the natives worked them into tools. (J. Herschel). Atlas, pp. 44, 45.

4. To-day, THE WORLD produces 175 tons<sup>c</sup> of GOLD a year (49 in U. S., 46 Australia, 15 Transvaal, 40 Russia in 1890; now Transvaal much more). In the same year (1890) the total production of IRON was 27 million tons, (U. S. 10, England 8, Germany 5, France 2). This enormous increase in the production of iron is directly due to chemical progress. The price in Germany was (1890) down to 12 dollars a ton.

5. THE UNITED STATES produced, in 1895, 71 tons of GOLD worth 47 million dollars, and 9.5 million tons of IRON worth 105 million dollars. Accordingly, the ratio of the weights of iron and gold possessing equal value is 60,000 to 1. With the progress of smelting this ratio has been rapidly increasing during the ages, and is bound to increase still more.

6. In addition to these two METALS, the ancients knew only five other bodies possessing metallic luster and malleability; namely silver, copper, tin, lead and mercury. For almost two thousand years these SEVEN METALS were compared to the seven planets and designated by the planetary signs: Gold, Sun; silver, Moon; quicksilver, Mercury; copper, Venus; iron, Mars; tin, Jupiter; lead, Saturn. Terms in common use still remind us of this comparison. Atlas, p. 43.

7. Chemists now designate the metals by the CHEMICAL SYMBOLS introduced by BERZELIUS and consisting of the first and the characteristic letters of their latin (or latinized) name. Thus gold (aurum), Au; silver (argentum), Ag; quicksilver (hydrargyrum), Hg; copper (cuprum), Cu; iron (ferrum), Fe; tin (stannum), Sn; lead (plumbum), Pb. In a like manner, sulphur is represented by S, Carbon by C, and Iodine by Io. Atlas, p. 22.

8. The seven old metals remain even to-day THE GREAT METALS in the economic life of nations. Thus the United States produced in 1895 in all 270.5 million dollars in metals, of which iron 105.2; silver 60.8; gold 47.0; copper 38.7; lead 10.7; zinc 6.3; mercury 1.3 million dollars. Here we have the big seven of old, with the exception of tin, replaced by the modern zinc.

9. These seven old metals are easily DISTINGUISHED. Mercury is a heavy liquid, silvery white. Tin and lead are readily fusible; color and gravity distinguish them: Sn, white, 7.2; lead, bluish-gray, 11.4. The three most lustrous and malleable metals melt in the blowpipe flame, and are distinguished by color and gravity: Cu, red, 8.8; Ag, white, 10.5; Au, yellow, 19.4. Iron is infusible in the blowpipe flame, grayish-white, and has G 7.8; it is also magnetic.

10. Zinc (Zn) was known to ALCHEMISTS in the 15th century; it is a metal, but malleable only at a moderate range of temperature (100 to 130 degrees); melts at 415, G 6.9; boils 940. The readily fusible and quite volatile metals Arsenic (As), Antimony, (Stibium, Sb) and Bismuth (Bi) are so brittle that they can be pulverized; color and gravity will distinguish them: As, corroding black, 5.7; Sb, is white, 6.7; Bi, reddish-white, 9.8. Probably at some temperature these will show malleability.

11. DURING LAST CENTURY the very heavy (21.5) white metal Platinum (Pt), infusible in the blowpipe flame, was found in Brazil. The lighter (11.4) companion Palladium (Pd) was distinguished by Wollaston, 1803. Nickel (Ni) and Cobalt (Co) are rare companions of iron, equally infusible in the blowpipe flame, almost equally magnetic, but heavier (8.8) and whiter; Ni corrodes green, Co pinkish-red. Manganese (Mn) and chromium (Cr) also resemble iron, but are not yet used as metals.

12. Near the beginning of the present century a number of LIGHT METALS (G less than 5) were discovered; the follow-

ing have lately come into use. Aluminium (Al) quite white, like silver, has F 625, G 2.56, and does not corrode in dry air. Magnesium (Mg), grayish-white, F 420, G 1.75; burns most brilliantly to a white ash when lit by a match. Finally the silver white metals sodium (Natrium, Na) and potassium (Kalium, Ka) cannot be kept in air, are lighter than water, in contact with which they burn.

---

NOTES 3.—The great IOWA METEOR (10:20 P. M., February 12, 1875) was seen throughout the territory extending from St. Louis to St. Paul and from Chicago to Omaha. Its explosion was heard over the ten thousand square miles of Iowa shaded on the map, p. 44.

The meteorites fell in Iowa County, Iowa, scattered over an elliptic area extending nearly ten miles from southeast to northwest, and almost three miles across at the widest. The greatest stones (all containing over ten per cent of native nickelliferous iron in granular form) fell between the seven towns of the Amana Colony; hence the name AMANA METEORITES. I made seven collections, aggregating over five hundred pounds; four of these groups are well shown on page 45 of the Atlas. The two largest (Nos. 22 and 33) were not my own property, but entrusted to me for study and protection. The largest stone weighs seventy five lbs. (No. 33); the smallest two oz. (No. 32).

The following specimens, arranged in decreasing order of weight, were presented by the author to the principal mineralogical museums of Europe: No. 1, Paris (5 kilos, nearly); 2, London; 11, St. Petersburg; 4, Vienna; 13, Brussels; 5, Copenhagen; 14, Harlem; 6, Berlin; 15, Paris (second specimen, over 2 kilos); 7, Christiania; 8, Stockholm; 16, Munich; and No. 9, Lausanne (1 kilo).

The specific gravity ranged from 3.45 to 3.50.

METEORITES, entering our atmosphere from space beyond, are the only cosmical substances accessible to the chemist; hence their extraordinary importance. They range from pure nickelliferous IRONS to STONES almost destitute of metallic iron.

The oldest COLLECTION of meteorites is at Vienna. It was mainly developed by Haidinger (p. 28), and is now again rapidly growing under Brézina. It contains 500 distinct localities, of which 320 are stones; the total weight is three tons and a half. The collection of meteorites at the Museum of the Jardin des Plantes at Paris was greatly developed under the care of the eminent Daubrée, and is now in charge of Meunier. The grand collection of the British Museum at London is in charge of Fletcher. The London collection is the richest, because of the vast ex-



tent of the empire in which the sun never sets, and because English intelligence is ever ready to part with British gold to secure prime materials for science. Thus they possess the largest meteoric iron from Cranbourne, Australia, weighing ten tons; and their gold secured the most remarkable Estherville meteorite (May 10, 1879) from this land of millionaires. However, this meteorite was drawn up from its wet hiding place for my study, before it left this country.

## 7. CALCINATION AND REDUCTION.

1. GOLD heated on charcoal, in the fusing point of the blowpipe flame, will promptly melt to a metallic globule, but suffer no other change. When cold, it retains the globular form, has all its original properties, and lost nothing in weight. It has been TRIED BY FIRE. (1 Pet. 1.7; Rev. 3, 18). It remains the king of metals; a metallic globule obtained by the blowpipe is still called a regulus, and pure metals are called reguline, as of old.

2. SILVER melts like gold, but loses slightly in weight; a small amount of a metallic calx is deposited as a reddish INCRUSTATION on the charcoal. Heat this incrustation for an instant with a good, steady, inner flame, and minute, brilliant white silver globules will appear. The calx has been reduced again to reguline silver. Mercury completely volatilizes in the blowpipe flame.

3. COPPER melts like gold and silver. The globule remains red in the inner flame, tinging that flame green, while in the outer flame the globule turns black on the surface. This copper ash, scraped off, gives reguline copper in the inner flame.

Most other metals are much more readily CALCINED, and correspondingly more difficultly REDUCED.

4. Exposing a fragment of LEAD on charcoal to the blowpipe flame, it melts almost instantly, boils, and burns with a bluish flame to a calx or ash (Litharge) which forms quite a

large yellowish, incrustation on the charcoal. If the outer flame is used for some time, the incrustation will be reddish (red lead), and all metallic lead will be calcined.

5. This lead incrustation, heated in the inner flame, almost instantly yields a multitude of minute globules of metallic lead (reguli), readily recognized as such by color, softness and malleability.

Thus lead is readily calcined in the outer, and reduced in the inner flame. This change from metal to calx, and reduction from calx to regulus, may be repeated any number of times.

6. Lead containing some silver will leave that silver as a pure regulus, while the lead is calcinated in the outer blowpipe flame. In this manner much of the silver has been extracted from argentiferous lead from time immemorial; the process is called CUPELLATION. The name litharge (lith-argyros, silver stone) still in use points to the antiquity of this process. On a porous support (bone ash cupel) it works better than on charcoal, the melted calx soaking into the cupel.

7. TIN heated on charcoal in the outer flame melts and forms a white incrustation due to its calcination. This incrustation can be reduced to a regulus, especially after mixing the calx with a little soda and borax. Aiding reduction to the metallic state, soda alone or with borax, is spoken of as a REDUCING FLUX.

8. A fragment of ZINC is so promptly calcinated in the outer flame that its fusion is usually not noticed. It burns with a brilliant green flame and deposits a large incrustation which (as well as the RESIDUE of calx left where the metal was) is infusible, yellow while hot, and turns white on cooling. This change in color can be indefinitely renewed by repeated heating.

9. MAGNESIUM burns with extreme brilliancy, leaving a pure white, infusible residue of calx. ALUMINIUM burns also, but much less readily; its calx is also white and infusible.

These white infusible masses cannot be reduced by the blowpipe, but are readily distinguished by igniting them after the addition of a drop of COBALT SOLUTION. The calx from aluminium will become deep blue, that from magnesium pale rose, while zinc calx treated in this way becomes green.

10. The metals As, Sb, Bi burn readily and leave an ash. The most volatile ARSENIC, emitting the odor of garlic, disappears, leaving but a slight white incrustation far away from the sample. ANTIMONY melts to a globule and burns with a white smoke, rising straight up from the sample when the flame is withdrawn; when the burning globule is dropped on the table, it breaks into many small globules, each leaving a white trail of the calx. BISMUTH gives a yellow incrustation. When reduced, both antimony and bismuth are brittle, distinguishing them from tin and lead.

11. IRON heated in the outer flame gives a black residue, no incrustation; when again exposed to the inner flame (best with soda) only gray, MAGNETIC grains or spangles are obtained. COBALT and NICKEL act in a like manner.

They are however readily distinguished by fusing a little of the calx into a borax bead. Iron will make the bead yellowish in the outer, colorless in the inner flame; nickel gives a brownish bead, and with cobalt the bead shows a splendid deep blue color. The chromium beads are green, those containing manganese are amethyst in the outer, colorless in the inner flame.

12. The light metals SODIUM and POTASSIUM should not be burnt in the blowpipe flame; it would be very dangerous. They leave white, fusible residues, coloring the flame yellow (Na) or purple (Ka).

Thus all metals may be readily distinguished in a few instants by the blowpipe, even if they are calcinated or otherwise combined. These fire-tests or PYROGNOSTIC CHARACTERS of the metals, should be familiar to all who wish to study chemistry. They are the most ready and distinct means for the recognition of the metals under all conditions.

## 8. ALLOYS AND AMALGAMS.

1. The different metals can be melted together in various proportions forming ALLOYS, several of which have been in common use from time immemorial, such as bronze and brass. If one of the metals is mercury, the alloy is called an AMALGAM.

2. The readily fusible white metals are very soluble in mercury. Lead, antimony, bismuth and even silver, dissolve so readily and abundantly in mercury as to cool the mass, over 20 degrees (down to 16 below zero). The tin amalgam is used as a coating on glass for mirrors.

Iron is insoluble in mercury; so are the other metals infusible before the blowpipe, like platinum. Accordingly, mercury is shipped in iron flasks, each holding 35 kilos.

3. Gold is about as soluble in mercury as silver. The GOLD AMALGAM is solid at common temperatures, and can be separated by wringing out the chamois into which the mercury and amalgam has been poured; the mercury will run through, the solid amalgam remaining. The amalgam loses about one third of its weight on heating, or contains two parts of gold to one of mercury.

4. The bulk of all the mercury produced (about 4000 tons a year) is used for the EXTRACTION of GOLD and SILVER. Gold sand is concentrated by washing, the lighter materials being removed farthest. When sufficiently concentrated, the remaining heavy material is treated with mercury, which dissolves the gold. The excess of mercury is separated as above from the gold alloy, which then by heat is freed from the mercury.

5. SOLDER, for tin ware, is an alloy of equal parts of tin and lead, melted together in an iron ladle. It melts at about 190 degrees, which is 40 degrees below the fusing point of tin, the most fusible of the two ingredients. In general, the alloys are more fusible than their constituents.

6. The most important of all alloys in the history of mankind is **BRONZE**, containing about one part of tin to nine of copper. In ancient days it was smelted direct from a mixture of copper and tin ores, or by adding tin ore to melted copper. By slow cooling it hardens, by sudden cooling it becomes malleable (contrast with steel).

7. The ancients, from the Egyptians to the Romans, made **WEAPONS, TOOLS** and **ORNAMENTS** of bronze. Until recently, canons were made of bronze; now it is used for statuary, bells, medals and ornamental work. The copper is first melted, then the tin added in reasonable excess, to allow for loss by combustion.

8. **BRASS** (yellow) is an alloy of two parts of copper with one of zinc. It can be cast, hammered, rolled and drawn and thus is most readily shaped into any form. It was used before zinc was known, by adding the mineral *cadmia* (a zinc ore) to molten copper. By adding an amount of nickel equal to that of zinc to the brass, German silver results.

9. **TYPE METAL** consists of lead about 4 and antimony 1 part, with some tin. It is very readily fusible, and expands upon solidification (as does water on freezing), thus filling the form exactly to the minutest detail.

Very fusible alloys contain bismuth. Thus Darcet's Metal, melting in the steam over boiling water, consists of bismuth 8, lead 5, tin 3 parts; it melts at 94 degrees.

10. The most characteristic modern alloy is **ALUMINIUM BRONZE** (copper 9, aluminium 1 part), which is very light and resembles gold in appearance. Ferroaluminium contains 9 iron to 1 aluminium; it is much stronger than the above.

11. Native gold generally contains some silver. Australian gold averages 7 per cent., Californian gold averages 12 per cent. of silver, and is light yellow. With about 20 per cent. it is called *Electron*, the *ASEM* of the ancient Egyptians. From this, pure gold or pure silver was obtained at will. The

alloys seemed to show that metals were variable and thus gave some encouragement to the alchemists.

12. When the Egyptians had learned to separate silver from gold, they dropped Asem from their list of metals. Their method of separation, described in the Leyden papyri, is essentially the same dry way process used till the present. The active agents were calcined green vitriol and salt, as in the ROYAL CEMENT of the alchemists.

## 9. ORES AND CLEAVAGE.

1. ORES ARE MINERALS FROM WHICH METALS CAN BE PROFITABLY OBTAINED. Every student in chemistry should know at least the principal ores from which already the ancients and the alchemists extracted the metals; he should be able to recognize them at sight and by handling them. To help him do so is the object of this lesson.

2. Ores are generally distinguished from other minerals by a HIGH GRAVITY (4 and over) associated with LOW HARDNESS. Very few have a hardness equal to glass (degree 5), that is, able to scratch glass and be equally scratched by it. Many have the hardness of copper (3) only. METALLIC LUSTER is frequent; in that case, the color is constant and therefore specific. If the luster is not metallic, the color is generally variable.



AGRICOLA.

3. THE BLOWPIPE will promptly reveal the presence and nature of the metal in the ore. It will also show whether the ore is a sulphide or not; the former emit the odor of burning

sulphur while heated. This test may be made by simply heating the mineral in an open glass tube, held slanting in the Bunsen flame. Some sulphides also yield a sublimate of white arsenic and give the odor of garlic.

4. Accordingly, the ORES are readily DISTINGUISHED as sulphides and free from sulphur. The last are either native metals or calxes. The first are either simple sulphides or contain arsenic also. We will give the principal distinctive properties for each of the common ores.

5. NATIVE METALS are distinguished by their luster and malleability (flattening under the blow of a hammer). They give no odor of either sulphur or arsenic before the blowpipe. Gravity and color distinguish them one from the other. G 17 to 19: Au, yellow; Pt, white; 11, Pd, white; 10, Ag, white; Bi, reddish gray and rather brittle; 8.5, Cu, red; 8, Fe, white, only in meteorites.

6. The CALXES are without metallic luster, either dull or sub-metallic. HARD enough to scratch glass (over 5) readily, are: G 6, CASSITERITE, brown, and brownish streak (streak is the color of the powder, or trace on rough porcelain), contains Sn; G 5, contain Fe; streak: Black, MAGNETITE; red, HEMATITE.

7. CALXES NOT HARD enough to scratch glass, but scratching copper readily, are quite numerous, and have all a specific gravity of about 4. Hence they are to be distinguished by color (first named) and streak (second): red, orange, LIMONITE (Fe); red, brownish-red, CUPRITE (Cu); reddish, orange, ZINCITE (Zn); grayish, white, SMITHSONITE (Zn); brownish, gray, SIDERITE (Fe); green, green, MALACHITE (Cu). GARNIERITE, the modern nickel ore, is green and harder than Malachite; blackish-gray, black, PYROLUSITE (Mn).

8. SULPHIDES HARD enough to scratch glass readily, but resisting the knife, have all marked metallic luster and therefore are easily distinguished by their color. Yellow, PYRITE



(Fe, no As). The following contain arsenic and are distinguished by their color and gravity: Gray, (6) ARSENO-PYRITE; white (8), LEUCOPYRITE, and red (7.5) NICCOLITE (copper nickel, the old nickel ore).

9. SULPHIDES, NOT HARD enough to scratch glass, readily yielding to the knife edge, have either brilliant metallic luster or not. By their gravity and color they are readily distinguished as follows; the metal they yield before the blowpipe being added. Brilliant metallic luster; gravity: 7.5, GALENITE, gray, Pb; 5, TETRAHEDRITE, gray, much As, some Ag; 4.5 STIBNITE, blackish-gray, Sb; 4, CHALCOPYRITE (copper pyrite), brass-yellow, Cu. Without metallic luster; gravity: 9, CINNABAR, red, Hg; 4, SPHALERITE, blackish to yellow, Zn; 3.5 ORPIMENT, yellow, As; 3, REALGAR, red, As. GRAPHITE (C) and SULPHUR (S) are readily distinguished from sulphides.

10. Almost every specimen of galenite shows many plane, brilliantly reflecting surfaces. If struck by a hammer, it will break according to such plane surfaces only, with extreme readiness; we say it has perfect CLEAVAGE. There will be seen three such cleavage planes, mutually under a right angle. This is most characteristic of galenite. Magnetite shows four cleavage planes; fine specimens of Sphalerite even six. Orpiment has one cleavage only, according to which it will split into thin foliæ. Pyrite is entirely destitute of cleavage.

11. Choice specimens, taken from the walls of some cavity, where the substances were free to grow, show beautiful geometrical forms, all bounded by plane surfaces only. Such specimens are CRYSTALS. Galenite, corresponding to its cleavages, shows cubes, often with the corners equally cut off (truncated); p. 66, fig. 2. Magnetite and Cuprite show octahedræ; p. 58, 59. Tetrahedrite shows modifications of half-octahedræ, or tetrahedræ; p. 66, figs. 16, 9. Hematite, especially from Elba, shows splendid six and twelve sided forms (Elba Roses), p. 57.

12. Pyrite quite frequently is crystallized. Its simplest and most common form is the cube, bounded by six equal squares (p. 66, fig. 1). Upon inspection these squares are usually found to be striated parallel to one side. Examining the three squares meeting at one corner, these striations will be found parallel to the three edges meeting at that corner, (p. 54, figs. 17 to 19). In many cases the edges are beveled, and finally show the so-called Pyritohedron (p. 66, fig. 21) bounded by twelve five sided faces.

---

NOTE. The portrait of GEORG AGRICOLA has been inserted in the text of this lecture. Agricola was called the father of mineralogy by Werner, a century ago. He was born March 24, 1494 at Glauchau, Saxony, and died in November, 1555, at Chemnitz, Saxony. He settled in the new mining town Joachimsthal, Bohemia, and studied everything pertaining to the rich silver veins which made that town and region flourish. His works on metals and mining are the first which have appeared during modern times; they are noted for thoroughness and accuracy. The portrait is a copy of Schrauf's, (Vienna 1894) which is a reduction from Sambucus, Antwerp, 1574, plate 38.

## 10. CRYSTAL GEMS.

1. The old egyptian list of metals contains blue (chesteb) and green (mafek) gems immediately after Gold (nub), Asem and Silver (hat), and followed by bronze (chomt), iron (men) and lead (taht). The Egyptians were familiar with the fact that copper tints fluxes blue and green; but they distinguished the genuine gems easily from the artificial by their hardness. Moses also was familiar with true gems. (Exod. 28).—Gems are sold by the CARAT which is one-fifth of a gramme.

2. THE TRUE GEMS (p. 46) are crystals of exceeding hardness. To be prized as jewels they must also be transparent and either absolutely colorless or finely colored. Hence, good instructive specimens are obtainable for study

at reasonable rates, while the price of the same materials fit for the lapidary may be beyond reach. Gems do not differ much in specific gravity; accordingly, this property is of little value in distinguishing them.

3. The gem crystals are generally well formed, and their DEGREE of SYMMETRY may be recognized without much difficulty. If the same face, as to inclination and position towards the direction of a more or less marked corner or prism, occurs twice only, the crystal is called rhombic, (pp. 61, 62); if thrice, rhombohedral, p. 57; if four times, quadratic, (p. 60), and if six times, hexagonal, (Beryl, p. 56). If the same crystal, held in two different positions, shows both rhombohedral and quadratic symmetry, it is called tesseral (pp. 58, 59). (For mono- and tri-clinic, see note).

4. The degree of HARDNESS of quartz is called 7; that of topaz 8, of corundum 9 and of the diamond 10. The most precious gems possess the hardness 8 and over; namely topaz 8, spinel 8, chrysoberyl  $8\frac{1}{2}$ , ruby and sapphire 9, diamond 10. Below these we have the emerald  $7\frac{3}{4}$ , zircon  $7\frac{1}{2}$ , turmaline  $7\frac{1}{4}$  and the "poor man's gems" garnet and quartz 7.

5. These gems are also CHEMICALLY divisible into the same two groups. All of lower hardness, including topaz, fail to dissolve in a bead of microcosmic salt in the blowpipe flame, precisely as do glass and other silicates; to that extent they are natural glasses, crystalized. But the harder gems, spinel, chrysoberyl and corundum (sapphire and ruby) do dissolve, and are not glass-like (silicates).

The diamond stands entirely by itself; it is combustible under special conditions.

6. QUARTZ crystals (p. 65) are quite abundant, and very often perfectly transparent (rock crystal); if purple, amethyst, if dark wine yellow, smoky quartz. Its hardness is taken as the standard 7. Gravity 2.7; no cleavage. Symmetry rhombohedral; commonly a regular six-sided prism, *r*, striated crosswise (Figs. 6, 7) dominates, terminated by the three

rhombohedral faces, P, usually alternating with a second smaller set of rhombohedral faces, Z. A little experience will enable any one to recognize the constancy of crystal form in the apparently infinite variety of appearances and linear dimensions.

7. The GARNET (p. 59) is recognized by its form, being generally a dodecahedron (bounded by twelve equal rhombs, d), inclined under a right angle over the long diagonal, and forming a rhombohedron of 120 degrees at the three sided corners. Garnets show many colors; the pyrope, used in jewelry, is deep red.

TURMALINE crystals have a dominant prism, striated lengthwise, surmounted by rhombohedral faces; usually only one termination shows, the crystals breaking readily crosswise. Colors varied, often in belts or zones.

8. THE ZIRCON (p. 60) is noted for quadratic symmetry only; fine transparent brownish and orange crystals are used under the name of hyacinth.

BERYLS (p. 56) are quite common and very large, forming regular six-sided prisms, terminating in a base at right angles thereto, and show cleavage after this plane. Fine beryls are always small and prized as AQUAMARINES when blueish; when bright green, they are the most valuable EMERALD.

9. The TOPAZ (pp. 61, 62; also p. 67, Fig. 43) forms a rhombic prism (M, l), striated lengthwise, and possessing perfect cleavage crosswise (i. e. basal, P); the crystals show generally only one termination, the basal plane with the domes f and y and the pyramid i. Yellowish colors are most common. The shade of color and especially the character or habitus of the crystals are peculiar to each principal locality, so that the expert can tell from the habitus and color whether the topaz came from Brazil, Saxony, Siberia or Japan.

10. SPINEL is tesseral, the octahedron (bounded by eight equal equilateral triangles, p. 58, fig. 1) dominating. CHRYSOBERYL (p. 62, Alexandrite) is rhombic; but its prism (119.8

degs.) is so nearly hexagonal (120 degs.) that it generally occurs in six-sided stellar combinations. A Russian variety, known as ALEXANDRITE, is emerald green in reflected, deep red in transmitted light, thus showing the Russian colors. Transparent specimens thereof form very valuable gems. Atlas, p. 53.

11. CORUNDUM (p. 56) is exceeded in hardness by the diamond only, so that it readily is distinguished from all other bodies. It crystallizes in rhombohedral forms, usually showing a double pyramid, terminated by a base, *o*. It shows perfect cleavage according to its base and a rhombohedron, *R*. Transparent crystals of corundum are next to the diamond in value; when blue they are called SAPPHIRE, when red RUBY. Good rubies have been made by Fremy. Impure corundum, containing hematite, is called emery, and used for grinding and polishing steel.

12. The DIAMOND is the hardest of all bodies; it crystallizes in octahedrae (p. 66, fig. 9) variously modified (figs. 11, 12), and has four cleavage planes parallel to the faces of the octahedron. Imperfect diamonds, unfit for jewelry, are called bort. Black pebbles of diamond hardness are called carbonado and used for rock drills. The price of good diamonds increases approximately as the square of the number of carats. Diamonds have been made by Moissan (p. 36).

---

NOTES—2. The cost of gems varies greatly according to quality. The following extract from the price list of a New York dealer is for "fair to good gems, neither poor nor the best." The price is given in dollars per carat; the order is that of our description.

Quartz: rock crystal  $\frac{1}{4}$ -1; amethyst  $\frac{1}{10}$ -1; garnet  $\frac{1}{2}$ -2; tourmaline 2-12; zircon 2-8; beryl, golden and aquamarines 1-8; emerald 10-80; topaz  $\frac{1}{2}$ -5; spinel 8-48; chrysoberyl 3-16; alexandrite 24-96. Corundum: sapphire 3-24; ruby 8-96. Diamond 50-150.

3. The important subject of Crystal Symmetry can only be approached by the beginner when aided by a good atlas of crystal forms. For that reason 18 plates of the admirable atlas of Nikolai von Kokscha-

row, accompanying his great work: *Materialien zur Mineralogie Russlands*, have been added in good photo reductions. In most cases each form is represented first in perspective and right below in horizontal projection; the first is marked by the number, the second by the same number and the word "bis" (twice, second). This second figure shows the symmetry undisturbed by perspective, and should be specially studied. Each face is generally designated by a letter.

In addition to the five degrees of symmetry specified, two lower forms exist, namely: MONOCLINIC, having only symmetry right and left, in pyroxene, p. 63 and orthoclase p. 64; and finally TRICLINIC, having no symmetry whatever, or being asymmetric, see Lepolith (really anorthite) p. 64.

9. Good specimens of topaz for the study of rhombic crystal form are comparatively cheap; the basal cleavage avoids the possibility of mistakes.

The three plates copied from Kokscharow show some of the finest topaz crystals in their true form, each face exactly as it is developed. The scale of our plates is almost one-half of the original; exactly 0.44 or nine-twentieths. See pages 61, 62, where the plates are designated by the letters a, d and f at the right hand top.

On page 61 (a and d) figures 58, 59 and 67 represent (half size) splendid topaz crystals from Nertschinsk, Siberia (Vol. III, p. 207). They are transparent, dark wine yellow. The crystal fig. 59 weighs 1.6 kilograms.

On page 62 (f) is given (fig. 76) the horizontal projection (half natural size) of the finest and largest topaz crystal yet obtained. It is 28 cm high, 16 and 12 cm across, and weighs 10.2 kilograms. Von Kokscharow (III 378) says: ". . . a topaz crystal of so extraordinary size and beauty as has never been seen before. This crystal belongs to the greatest rarities of the mineral kingdom, on account of its extraordinary magnitude, perfection of crystallization, fine color (dark wine yellow) and transparency." It was found in the Nertschinsk region, in the mountains near the Ululga river, Transbaikalia, Siberia; was presented to Emperor Alexander II in 1860, and is deposited in the Mineralogical Museum of the Mining Institute of St. Petersburg.

10. The group of Alexandrite crystals represented (p. 53) is one of the most magnificent specimens of native crystals (v. Kokscharow, Vol. IV, p. 62). The group contains 22 large and finely formed twin crystals; the group is 25 cm long, 14 cm high and 11 cm wide, and weighs over 5 kilograms.

THE GEMS. Page 46, shows the common crystal form of the following: 1, diamond; 2, sapphire; 3, ruby; 4, amethyst; 5, emerald; 6, garnet; 7, aquamarine; 8, topaz; 9, peridot or olivine, chrysolite; 10, rock crystal; 11, turmaline. This plate is a half-tone reduction from the fine colored plate V of Simonin, *Les pierres*, Paris, 1869.

## 11. CRYSTAL STONES.

1. THE RECOGNITION OF ANY MATERIAL by means of its physical properties is a habit that must be cultivated by every one who would study chemistry successfully. Incidentally the student becomes practically acquainted with a number of those minerals on which the chemist depends for his materials—and even for the very ideal of chemical individuality.

2. The following dozen STONES should be so familiar to every student that he can recognize them promptly in any of their varied forms. As a group they are not as hard as the gems, nor as heavy as the ores. H 6 and G 4, are the limits. The dozen selected are the most important practically, and the best marked physically and crystallographically. Good specimens can be had at comparatively little outlay; many can be collected.

3. To recognize a substance, its properties should be observed in a DEFINITE ORDER. First (by sight) luster, then color and streak; next (by handling), hardness and by mere lifting an estimate of the specific gravity is obtained. Then the specimen—if not a crystal—should be broken by a blow; that will reveal fracture or cleavage; in the latter case, the number, relative position and degree. Finally, if crystal faces visible, they should be examined with a view to determine the symmetry of the crystal. In that case, cleavage planes are often revealed by existing cracks.

4. The last five of the minerals selected are SILICATES, that is, they leave an insoluble silica skeleton in the microcosmic bead (10, 5); they are among the most common constituents of the hard rocks, such as granites. The others are not silicates. The first alone is soluble, its taste reveals its nature, salt; the merest trifle of it tinges the blowpipe flame persistantly and intensely yellow (Na). The next five tinge the flame orange, appearing siskin-green through a green glass; they contain calcium (Ca). The heaviest tinges the flame yellowish green; it contains the metal barium (Ba).



## 5. TABULAR VIEW OF THE PROPERTIES OF A DOZEN STONES—

No.	NAME.	H.	G.	Cleavage.	Crystal Symmetry.
1.	HALITE,	2	2.2	3 pfct., 90 degs.	Tesseral.
2.	GYP SUM,	2	2.3	1 em., 2 pfct.,	Monoclinic.
3.	CALCITE,	3	2.6	3 perfect, 105 degs.	Rhombohedral.
4.	ARAGONITE,	3½	2.9	1 imperfect.	Rhombic.
5.	FLUORITE,	4	3.1	4 perfect, octah.	Tesseral.
6.	APATITE,	5	3.1	1 imperfect.	Hexagonal.
7.	BARITE,	3	4.5	1 pfct., 2 less so.	Rhombic.
8.	MICA.	2	2.9	1 eminent.	Six-sided.
9.	AMPHIBOLE,	5½	3.2	2 pfct., nearly 120 degs.	Monoclinic.
10.	PYROXENE,	5½	3.3	2 pfct., nearly 90 degs.	Monoclinic.
11.	FELDSPAR,	6	2.5	2 pfct., nearly 90 degs.	Mono or triclin.
12.	QUARTZ,	7	2.7	no cleavage.	Rhombohedral.

6. All of these stones are destitute of metallic LUSTER, that property being peculiar to metals and ores. The luster is dull or vitreous according to the perfection of the specimen. If ONE CLEAVAGE eminent, so perfect that it can be split into thin leaves (Nos. 2,8) the luster will appear pearly, which is noted even on the best cleavage of feldspar (No. 11.)

7. These minerals are generally colorless or white; but as they have no metallic luster, their COLOR VARIES according to impurities admixed, whether organic or inorganic. Thus Halite (Rock Salt) and Fluorite (Fluorspar) show beautiful colors: yellow, red, green, blue, mostly due to organic matter, destroyed by ignition. Pyroxene (augite) and amphibole (hornblende) are generally green to black, from iron silicates. Quartz and calcite show also most of the colors of the rainbow.

8. Contact with the tongue reveals the only SOLUBLE mineral in the list, HALITE. Hardness 2, indentable by the finger nail, singles out gypsum and mica. Of these two, only GYPSUM occurs massive and fibrous; when foliaceous, its folia are flexible, but not elastic, while MICA always is foliaceous and elastic as well as flexible. [CRYOLITE from Greenland, has greater gravity (3) and is insoluble in water; otherwise it might be mistaken by hardness and cleavage for poor specimens of rock salt. See p. 51.]

9. Copper hardness (3) gives the three species Calcite, Barite and ARAGONITE (p. 67, fig. 55). This latter is very rare, almost destitute of cleavage, while the other two possess perfect cleavages. BARITE is readily distinguished by its high gravity, which has given it the common name Heavy Spar. By cleavage it yields right rhombic tablets of 101.7 degs. The lighter is CALCITE or calcareous spar, the most common of all minerals, which will receive special study further on. It effervesces with vinegar.

10. FLUORITE (Fluorspar) and APATITE (p. 67, fig. 37) are not scratched by copper. Fluorite generally shows its cleavages readily, while apatite practically has no cleavage. The four cleavages of Fluorite equally developed yield a tetrahedron (p. 66, fig. 16); splitting off the corners also, the regular octahedron (fig. 9) results. Fluorspar crystallizes beautifully (figs. 1, 5, 7, 14, etc.) and shows many fine colors; it is the ERZBLUME (ore blossom) of the old miners, accompanying valuable ores.

11. The silicate stones are easily distinguished by hardness and cleavage combined. One eminent cleavage, MICA (isinglass); no cleavage, QUARTZ, if hardness 7 (good file). Hardness below this, but the specimen scratching glass quite readily, showing two cleavages under a right angle: FELDSPAR (p. 64: Orthoclase and Anorthite, here called Lepolith) which is reddish or whiteish, except in the bright green Amazone stone. AUGITE (Pyroxene, p. 63) and HORNBLENDE are not as hard, but heavier, blackish and greenish colors prevailing; only if showing cleavage, can they be distinguished, except that fibrous varieties are hornblende.

12. CALCITE (p. 65) exhibits a thousand modifications (secondary forms) of its rhombohedron, P, of 105.1 degrees, according to which all are broken up by the cleavage planes parallel to the three faces of the rhombohedron meeting in one corner (HAUY, p. 55). The most common secondary forms are the Scalenohedra (r, figs. 15 to 21, Dogtooth Spar); next thereto the hexagonal prism, c, and the obtuse rhombohedron,

g (Nailhead Spar). Marble is crystalline (saccharine marble); variegated marble may be massive. Limestone is the most common form. The most perfectly transparent cleavage pieces come from Iceland (Iceland Spar); next in perfection are the spars from Lampasas, Texas.

## 12. ROCKS AND VEINS.

1. LIMESTONE generally is stratified, forming banks or strata of varying thickness, apparently deposited in a primeval sea. The strata have since, in many places, been tilted and broken. Extensive deposits of limestone occur, hundreds of feet in thickness, and for hundreds of miles in extent. They furnish locally fine building stone and material for burning lime.

2. Many LIMESTONES are quite hard, some even crystalline; but all effervesce readily with vinegar. The beautiful white MARBLE of Carrara has been quarried for statuary and ornamental work since the days of the Romans, (p. 51). The Greeks obtained a superior, more fine grained marble for their statuary and monumental buildings from the island of Paros. Gypsum also forms valuable rock deposits; easily distinguished by yielding to the finger nail and not effervescing with vinegar.

3. SANDSTONES consist of grains of sand (irregular fragments of quartz) held together by some stony cement, often calcareous and effervescing with vinegar. These stones are also stratified, but less extended than the limestones; they vary exceedingly in their characters, as to color, grain and durability of the cement. Many localities offer excellent building stones (Strasburg Munster). The building stones quarried in the United States during 1895 had a value of 35 million dollars.

4. CLAY like deposits form extended strata, differing in consistency from moist, plastic clays to shales and slates (for

roofing). When heated to redness, clays lose their water, shrink and become hard (brick, pottery.) In a bright white-heat most ordinary clays will show signs of fusion; the purest clays (white, free from iron, lime, etc.) resist furnace heat, are called fire clay, and serve for crucibles, finer pottery, to porcelain. All these clay rocks contain aluminium for they will (after removing iron, etc.) give the blue cobalt reaction (7.9).

5. These common stratified rocks—limestones, sandstones and shales—are resting upon and at times tilted up by the the two principal crystalline siliceous rocks, the graystones (GRANITES) and the GREENSTONES (hornblendic and basaltic rocks). In granite the three constituent minerals (mica, feldspar and quartz) may be distinguished without much difficulty. The greenstones are heavier, containing more iron.

6. During great convulsions, the rocks, whether stratified or not, have been cracked, deep fissures running nearly parallel have been made. In the course of time, nature has healed these wounds, filled up these crevasses in various ways, by materials drawn from the adjacent rocks (the country) or from the depths. Such filled up deep crevasses are called veins (p. 47), especially if they contain ores with the other minerals or veinstones (gangue).

7. The true veins extend indefinitely downwards; their direction on the ground is called their strike, their inclination, dip. The most common veinstones are quartz, calcite, fluorite and barite. These gangues, as well as the associated ores, are often quite symmetrically distributed across the vein, that is, if from the left the order of minerals be a, b, c, d, it will be the same from the right side of vein. See p. 47.

8. If, after a set of veins has formed, like convulsions take place again, another set of cracks may result, leading to another set of veins with other gangue and other ores, CROSSING the first and older ones, which thereby may have been greatly displaced. (See right side, p. 47). At Ehrenfriedersdorf, a set of silver veins run from north to south, while the tin veins run from east to west.

9. The discovery of rich veins in a new country is a matter of luck. The crowd drawn by the story makes a careful and extended search (prospecting) and is followed by the general settler. In a few years, the treasure found, has added a rich and populous state to civilization. The words California, Colorado, Australia, Transvaal, all tell the same story. In Antiquity, similar effects of mining are recorded.

10. One of the most remarkable stratified rocks is stone coal, H 2, G 1.5 and less, black combustible (p. 48). Anthracite (hard coal) gives no volatile matter (bitumen) when heated in a tube; the other coals give up to 50 per cent. bitumen, and burn with a luminous flame. Asphaltum and Petroleum are essentially natural bitumens, with but little fixed carbon. Stone coal supplies our industries with heat and power; largely replacing the slave labor of earlier civilizations. The United States produced 265 million dollars worth of mineral combustibles in 1895—as much as their total production of metals.

11. Iron ores also occur as rock deposits. The magnetite (p. 52) and hematite deposits of Elba formed the center of metallurgy of Antiquity. We have corresponding deposits in Missouri (Iron Mountain, Pilot Knob) and especially on Lake Superior (Marquette Region). In parts of England, iron ore, coal and flux occur in neighboring strata, greatly favoring the smelting of the iron.

12. SALT is obtained by the evaporation of sea water (France, p. 50, top); from salt springs (Michigan, New York); and above all as rock-salt. The Stassfurth rock-salt deposit is over three thousand feet thick. That at Vilisca—over one thousand feet thick—has been mined for centuries. At Cordonna, Spain (p. 50), rock-salt is quarried from a deposit reaching over five hundred feet above ground. These deposits are associated with gypsum and other salts of sea water, proving them to be the result of evaporation of bays of a primeval ocean, or inland lakes (Dead Sea, Great Salt Lake).

## 13. SALTS AND SPIRITS.

1. The ancients distinguished a number of substances resembling rock-salt in appearance, solubility, and marked by some peculiar taste; the term SALT has been used to designate all materials of this kind. The most important salts have been in use for two thousand years; surely, every student of chemistry should be able to recognize them.

2. Already the Hebrews used two very soluble salts effervescing with vinegar. Neter (to effervesce) was found in lakes of northern Africa, and is permanent in air; we call it SODA. The other, borith, was obtained by lixiviating wood ashes; it is our very deliquescent POTASH. Both of these substances are non volatile or fixed. A very volatile salt of this kind (*spiritus urinæ*) was at an early day obtained from putrid urine; we call it Ammonium Carbonate, and obtain it from stone coal (gas works refuse, tar water).

3. ALUM is a styptic salt. When heated in a tube it gives off much water and leaves a light, white, ash-like residue, called burnt alum. Accordingly, the ancients said alum consists of water and earth. The old VITRIOLS (glass-like) are similar salts, styptic, but heavier and yielding much less water; the one is pale GREEN and gives iron before the blowpipe, while the other is deep BLUE and yields copper. Pyrites weathering give green vitriol, while blue vitriol results from the weathering of copper pyrites (9. 8).

4. Our nitre or SALTPETRE (*sal petræ*) was found as crusts on rocks in caves of Asia Minor; it is distinguished from the preceding salts by violently deflagrating on glowing charcoal, showing its leading character of supporting combustion. BORAX on the contrary, melts quietly to a colorless drop or bead; it readily dissolves metallic ashes, forming characteristic colors therewith. It is also a most useful flux in smelting.

5. Limestone when burnt leaves quick LIME, which heats up greatly with water; yielding slacked lime which is slightly soluble in water (Limewater) and very CAUSTIC (corrosive to the skin and organic tissue). While limestones effervesce with vinegar, slacked lime does not. Concentrated solutions of the effervescent soluble salts (2) yield with slacked lime, upon decantation, the most caustic liquids known, the CAUSTIC ALKALIES.

6. SAL AMMONIAC first came from Egypt in fibrous cakes, already described by Dioscorides; the crude salt of to-day has the same characteristic fibrous structure. When warmed with slacked lime, pungent spirits of ammonia are abundantly produced and readily taken up by water, giving our Aqua Ammoniae, the volatile alkali.

7. The ancient chemists studied the properties of all materials at high temperatures. They distinguished the very volatile substances as we do. The volatile principle collected in a distilling apparatus they termed SPIRIT, independent of the special property, which might be acid, like vinegar, neutral, like water, or alkaline, like ammonia. Litmus turns red with acids, blue with alkalies, and remains unchanged (blue or red) with neutral substances.

8. VINEGAR (acetum) is the only acid known to the ancients; it resulted from light wines exposed to air, turning sour (*vin aigre*, french). We have used it to recognize limestone, marble, soda, by the effervescence it produces. Vinegar dissolves lead, yielding SUGAR OF LEAD, readily soluble in water. Such a solution gives an abundant white precipitate with vitriol and alum solutions, even when much extra vinegar has been added. None of the other salts show this behaviour (reaction).

9. Alum mixed with nitre and heated gives the strongly acid SPIRITS OF NITRE, our nitric acid—the “first water” of the alchemists. This corrosive liquid stains the skin and wood yellow, and dissolves copper readily, while abundant and



very noxious red fumes (rutilant vapors) pass off. Silver also dissolves in this acid, leaving white transparent crystals—lunar caustic, lapis infernalis—our SILVER NITRATE.

10. Alum and salt (murias) heated in the same manner yield the less corrosive SPIRITS OF SALT, our muriatic acid. It is easily distinguished from the preceding acids by giving a white, curdy precipitate with silver nitrate; which precipitate is readily dissolved by aqua ammonia. Accordingly, silver is insoluble in muriatic acid.

11. Mixing both salt and nitre with alum, heat drives off the most corrosive acid, AQUA REGIA, so called because it dissolves even gold, the king of metals. These acids were quite generally used by chemists in the days of Geber, more than a thousand years ago. Aqua regia was called the “second water” by the later alchemists.

12. Intensely heating alum (or any vitriol) alone (or with dried, pure clay) we obtain SPIRITS OF VITRIOL, our sulphuric acid, or oil of vitriol. It chars most organic materials (wood), and gives the same white precipitate with sugar of lead which we obtained with alum and vitriol solutions.

At present, the term spirit is restricted to the distillate from wine and similar liquids; our alcohol is spirits of wine, spiritus vini.

---

NOTES. Section II is in accordance with current information, accepting the works of Geber as they exist in latin to be genuine, due to the arab Djaber (eighth century). But Berthelot has published the original text in arabic and finds (*Comptes Rendus*, T. 116, p. 1166-1171; 1893) that the latin works accepted for centuries as the translation thereof, are works of European chemists of much later date; that the arabs did not add to the chemistry of the Greek school. Consequently, that “thousand years ago” will have to be cut in two, leaving say half a thousand years.

## 14. SOLUTION AND CRYSTALLIZATION.

1. THE OCEAN is the greatest residual solution on the globe. The taste of its water reveals the presence of common and bitter salts. By evaporation sea-salt is obtained therefrom. The great (rock) salt deposits have undoubtedly been formed in bays periodically in narrow communication with the ocean (12, 12; Atlas, p. 50). Sea water contains  $3\frac{1}{2}$  per cent. of salts, varying slightly in different regions. Forchhammer, 1864.

2. SOLUTION is the conversion of a solid into a liquid by means of a liquid. The liquid used is called the solvent, the liquid resulting is called the solution. The word solution thus is used both for the operation and the result. A solution is saturated, when in contact (aided by repeated shaking) with the finely pulverized solid, it does not take up any more thereof. Concentrated is a solution approximating saturation; dilute when remote from it. Water is the most common solvent; alcohol, ether, and other volatile liquids are also used.

3. THE SOLUBILITY of a solid is the weight thereof dissolved to a saturated solution by a unit of weight of solvent (Gay-Lussac, 1819). It may also be defined as the weight of the solid contained in a unit of weight of the saturated solution (Etard, 1894). For practical purposes, the STRENGTH OF ANY SOLUTION (whether saturated or not) is usually given by stating the weight of solid per unit of volume of the solution; that is in milligrammes per cubic centimeter or grammes per Liter.

4. THE SOLUBILITY INCREASES WITH THE TEMPERATURE, as shown by the diagrams, p. 70. For alum, nitre and blue vitriol dissolved in water, the increase is very rapid, the Gay-Lussac curves rising steeply. Salt shows but a very slight change in solubility. The Etard lines, p. 71, are straight, or consist of several straight lines, the last section

(except for sulphates) running to the melting point. All chemistry in the WET WAY is but an application of the facts of solubility.

5. When a given solid is divided, the surface increases rapidly, while the weight remains unchanged. As solution can only take place at the surface of the solid in contact with the solvent, it follows that PULVERIZATION must greatly accelerate solution. Solids are first broken with hammer and anvil, then crushed in a diamond mortar (steel socket with steel pestle), and finally ground thoroughly fine in appropriate mortars (porcelain, agate).

6. WARMING the finely pulverized solid with a reasonable excess of solvent will effect rapid solution of all that is soluble. Any insoluble impurities will remain in the solid state. They can be removed by DECANTATION after the solution has been standing undisturbed to permit the solids to settle; or better and more rapidly, they are removed by FILTRATION through a porous insoluble solid, usually filter paper, supported in a funnel of 60 degrees aperture.

7. A hot, concentrated solution set aside will COOL slowly, and generally soon show the growth of beautiful CRYSTALS, the solubility diminishing as the temperature sinks. With an almost boiling saturated solution of nitre, a half dozen consecutive crops of bulky masses of silky crystals may be obtained by as many consecutive decantations, showing most strikingly the enormous decrease of solubility of nitre upon cooling.

8. While the gradual cooling of a hot, concentrated solution gives rapidly large groups of crystals, the most perfect crystals are generally obtained from saturated solutions by SPONTANEOUS EVAPORATION, in crystallizing basins and dishes of glass or porcelain. On a small scale, watch glasses answer admirably. For work with the magnifier and the MICROSCOPE, a drop of solution on the microscope slide is sufficient. Creeping is avoided by a line drawn with paraffin.

9. By careful work a COLLECTION OF CRYSTALS of the more common substances may thus be obtained. The best crystals are comparatively small, and require a magnifier for close study. A trifle of wax, rolled on the head of a pin, serves to support the crystal. The pin stuck into the cork of a specimen tube mounts and protects the crystal quite nicely. A paper strip as wide as the cork is long, around the tube, forms the proper label.

10. The study of this subject is very much facilitated by procuring at drug stores a few LARGER CRYSTALS that can be picked out from a drawerful of blue vitriol, alum, nitre, yellow prussiate of potash, potassium sulphate, and the like. Rock-candy, in large crystal groups on strings, is also obtainable at candy stores. A few native crystals from dealers in minerals will greatly add to the value of the collection.

11. The operations of solution, filtration and crystallization are employed not only in the laboratory, but in chemical works to obtain pure products from impure raw materials (REFINING). Many of these raw materials are transported from hot or desert regions to Europe and the United States to be refined; salt-peter from India, borax from the dead valley of Arizona (formerly from Thibet to Venice), Chili saltpeter from South America, raw sugar from the tropics. Alum and blue vitriol works are among the oldest establishments producing pure chemicals.

12. Most soluble substances are associated not only with insoluble materials removable by filtration, but also with substances merely differing in solubility. The less soluble will crystallize first, the most soluble last; so that by setting aside of the first crop of crystals, and decanting before the substance wanted is all deposited, very pure materials are obtained. This process of FRACTIONAL CRYSTALLIZATION is one of the most simple and effective means for obtaining pure chemical individual substances.

## 15. CRYSTAL DESCRIPTION.

1. Magnificent specimens of CRYSTALS are found IN MINERALOGICAL MUSEUMS—and beautiful, though smaller, crystals of the most varied kind are MADE IN THE LABORATORIES. But their forms seem bewildering; no two crystals of the same substance appear to be exactly alike.

2. The ancients were familiar with the large quartz crystals of the Alps and the splendid blue vitriol crystals made in Spain. Pliny speaks of both; the former he considers ice (KRYSTALLOS, in Greek) so hard frozen that heat cannot thaw it (Hist. Nat. 37, 9), the latter he believes to be a glass vitrum, hence our word vitriol (Hist. Nat. 34, 11). It is only in modern days that the characteristic, fixed features in this form of crystals have been discovered. Accordingly we now can describe a crystal in such a way that its form can be identified and recognized by that description.

3. The Dane STEEN (or Steno) discovered (1669 in Italy) that while the linear dimensions of the six-sided quartz crystals varied infinitely (see p. 65) the angles between adjacent faces of that prism (rr) are constant, always exactly 120 degrees. Crystallographically, as to these INTER-FACIAL ANGLES, the quartz prism therefore is a REGULAR hexagon of 120 degrees. ROME DE L'ISLE (p. 54) and especially HAUY (p. 55) have laid the foundation of crystallography upon this law of Steno.

4. A CRYSTAL IS A POLYHEDRON FORMED SPONTANEOUSLY. This is the best and most simple definition that can be given. Its expresses the two fundamental facts, that crystals are bounded by plane surfaces called faces, and form without external influences, the substance being left entirely to itself. The line of intersection of two faces is called an EDGE. The point where three or more faces meet is called a CORNER.

5. Three or more faces having their edges parallel constitute a ZONE or PRISM. This prism is limited or cut off by one or more faces. If one face, it is called the BASE—right if at right angles to the edges, oblique if not. If the prism is cut off by two faces under an angle, as the roof on a house, these faces are called a DOME, also right or inclined, according as the ridge is perpendicular or not to the edges of the prism. If limited by three or more faces, the prism is said to be surmounted by PYRAMID.

6. The general appearance of a crystal is distinguished as TABULAR or PRISMATIC, according as two dimensions or one only predominates. If a corner or edge is replaced by a face, it is said to be TRUNCATED. If an edge is replaced by two faces, it is BEVELLED. The general predominance of a particular set of forms is called the HABITUS, and depends on the special conditions under which the crystals grew. See 10, 9.

7. The interfacial angle of a crystal can be determined with sufficient accuracy for all purposes of identification by my diagram GONIOMETER (p. 68) for student's use. Hold the edge of the crystal so that it appears as a point, and the two faces as lines—then the edge will be vertical to the paper goniometer, and it will be easy to find the angle most nearly identic with the interfacial angle concerned.

8. The crystal is held mounted on a pin or by means of forceps, and the eye may, for small crystals, be assisted by a magnifying glass of low power, that is, if long focus. Both large and small crystals are readily measured in this manner. After some practice, the nearest degree can be ascertained, though in description the TENTH of a degree will be stated for reference. Thus calcite is about 105 degrees; exactly 105.1 degrees.

9. BLUE VITRIOL (p. 68) crystals show the dominant zones MT 123.2, PT 127.7 and MP 109.2. In the first zone the faces *n*, *l*, *r* replace edges, so that Tr 110.2, Tn 148.8, Mr 126.7. Also Pn 120.8 and Pr 103.4.

Special characters: Crystals tabular after M; face T looks rectangular; face N is frequently striated parallel to edge MT; and face P in coarse crystals shows curved projections due to disturbed rapid growth. These forms are evidently triclinic, destitute of symmetry; 10, 3, note.

10. NITRE (p. 68) forms right prisms, M M'b, very nearly hexagonal; MM' 119.4, Mb 120.3. The right dome D measures 109.8 and Db 125.1. Crystals often tabular after b. ALUM is octahedral (O) with corners (hexahedron, H) and edges (dodecahedron, D) truncated. OO 109.5, OH 125.3, OD 144.7, and HH 90.0, DD 120.0. Crystals commonly grow resting on a face of the octahedron, and thus show rhombohedral appearance, the three D forming a rhombohedron of 120 and the three H one of 90 degrees.

11. THE FERROUS SALT (hydrated ammonio-ferrous sulphate) forms tabular crystals, the oblique base P dominating and striated. The prism MM' about 109, and MP=MP' about 105 degrees. The characteristic triangular truncatures q form Pq about 155 degrees.

These crystals form very readily by mixing strong solutions of ammonium sulphate and of ferrous sulphate (green vitriol); even a drop each on the microscope slide will suffice. This double salt is permanent in air; green vitriol is not.

12. The ferrous (pale green) solution may be replaced by nickel (deep green), cobalt (pink), manganese (pale rose), copper (deep blue), or the colorless solution of magnesium, zinc or cadmium sulphates. In all cases, these solutions will, with ammonium sulphate solution, give crystals of the same general form and nearly the same angles; such compounds are called ISOMORPHOUS. The habitus may be more prismatic or more tabular, according as MM' or P dominates. Isomorphism was discovered by EILHARD MITSCHERLICH (1794-1863); portrait p. 34.



## 16. MARBLE AND FIXED AIR.

1. CALCITE in all its natural varieties, down to the common limestone, has the property of promptly effervescing with vinegar; a drop of vinegar placed on the specimen produces the apparent boiling up (11,9). In a test tube this shows better; in large cylinders and flask the phenomenon becomes very striking. It is also advisable to take a common mineral acid, like muriatic or nitric acid instead of vinegar. Sulphuric acid cannot be used, giving a precipitate with lime solution.

2. TO STUDY THE GAS set free in this effervescence, it is necessary to produce it in quantity and to collect it. The most convenient generator is Kipp's, because it will yield the gas exactly as it is required. The upper compartment is charged with clean fragments of marble as large as can be introduced through the tubulature. The acid is dilute muriatic, 3 water to 1 acid. We remove the lower glass stopper, replace it by a rubber stopper (well tied or wired) connected with rubber tube, as shown. Then the pressure can be promptly released at the close of the working hours.

3. THE GAS is drawn by slightly turning the delivery stopcock. It may be collected in cylinders over the pneumatic trough or in empty gas washing bottles; best the Drechsler form made entirely of glass. A series of such cylindrical washing bottles may be connected by rubber tubes and thus the different reactions of the gas shown at one view. These cylindrical bottles are easily detached by the ground joint, so that the reagents can be introduced at any time.

4. COLOR, ODOR, TESTS. The gas collected over the water or in the washing cylinders cannot be distinguished by sight from the air surrounding the apparatus—it is colorless. Nor has the escaping gas been recognized by odor—it is odorless. In a wash bottle containing blue litmus, a wine red tint

is produced as the gas passes through—it is soluble in water, and that solution is an acid. In another cylinder, lime water becomes turbid (white precipitate), which increases in amount, finally diminishes again, and dissolves.

5. This solution, exposed to the air in a shallow vessel, gradually deposits microscopic rhombohedral crystals, exactly of the same form as the calcite rhombohedron of 105 degrees. They effervesce with acids, give the orange tint to the blow-pipe flame, exactly as calcite; they are ARTIFICIAL CALCITE. They show beautiful colors in the polarizing microscope.

6. THE GAS IS decidedly HEAVIER THAN atmospheric AIR; for it can be poured out of one vessel into another, exactly like water. A little lime water in the lower vessel becomes turbid, especially after shaking. A burning taper at the bottom of the lower cylinder will be extinguished, as the gas is poured into that cylinder—the same as if the taper were lowered into a vessel filled with the gas. The gas does NOT SUPPORT COMBUSTION.

7. PROPERTIES. The gas set free by an acid acting on calcite thus is colorless, odorless, heavier than air, does not support combustion; it is soluble in water, forming an acid, makes lime water turbid, an excess redissolves the precipitate, and from that solution the original calcite deposits in perfect rhombohedral crystals. This gas is evidently contained (fixed) in all forms of calcite; it was called FIXED AIR by Black of Edinburgh (1755), who first most thoroughly studied it.

8. This gas was first produced by VAN HELMONT (1577-1644), who introduced the term GAS; really spirit, ghost (engl.), ghoast (dutch), geist (german), gast (anglo-saxon). He called it gas sylvestre (spiritus sylvestris) or wild, savage gas, because he was unable to tame and control it, so as to collect and handle it. (See portrait, p. 30). Since Black, it has been called carbonic acid—but the dry gas itself has no acid properties. Then it was called carbonic anhydride, and

now it is quite learnedly called carbon dioxide! Bergman (1774) called it *acidum aëreum*.

9. BURNING CHARCOAL in a current of air, the product of combustion will show all the properties of fixed air; hence, fixed air contains carbon. In this experiment the charcoal is heated in a tube of Bohemian glass connected with the Drechsers, which are attached to an aspirator, producing the current of air. Air exhaled shows like properties; so does air from fermenting grape juice.

10. Fixed air has been LIQUEFIED to a limpid, colorless liquid by cold and pressure (Faraday, 1823); but no amount of pressure will liquefy it above 31 degrees. That is, above 31 degrees it is a true, non-liquefiable gas; below 31 degrees it is a condensable vapor. This limiting temperature between vapor and true gas is called the CRITICAL TEMPERATURE. The pressure sufficient to liquefy it at that temperature is 73 atmospheres. At  $-78$  degrees, fixed air CRYSTALLIZES to white, snow-like masses (Thilorier, 1835).

11. LIQUID FIXED AIR (liquid carbonic acid) is now produced in chemical works and sold in steel cylinders to various industries. The solution of fixed air in water, made strong by using from 2 to 5 atmospheres pressure, is used as a refreshing beverage (soda water); it is also produced in the portable fire-extinguishers and chemical fire engines. Many natural spring waters are also strongly carbonated, that is, impregnated with fixed air.

12. RAIN DROPS ABSORB FIXED AIR while falling, and while sinking through the soil. Reaching the rocks below, the water will slowly dissolve limestone, become hard—depositing kettle stone when boiled. Such rock-water, reaching fissures or cavities, will lose its fixed air and deposit the limestone it held in solution as calcite, often finely crystallized. Thus chemical changes (METAMORPHOSES) are going on in the depths of the earth.

## 17. ZINC AND INFLAMMABLE AIR.

1. Iron is insoluble in water; iron pipes are used for water conduits in cities. But if to the water standing over scrap iron, oil of vitriol be gradually added, effervescence will promptly start up; an inflammable gas of unpleasant odor will escape in abundance. Paracelsus (1493-1541) has first described this quaintly: Air rises and bursts forth like a wind. BOYLE (1626-1691) first collected this gas. See portrait p. 21.

2. Cavendish (1731-1810) first carefully studied this gas which he called INFLAMMABLE AIR. He found it colorless and odorless (when pure); the lightest of all gases (1765); inflammable, producing water when burning. With air it forms an explosive mixture. Hence, great care is required when handling this gas near any flame; the explosions are violent, so much so that Lemery thought (1675) thunder due to the "fulminations" of this gas.

3. TO GENERATE INFLAMMABLE AIR in quantity, charge a Kipp with ordinary granulated zinc and dilute muriatic acid. Collect a cylinder full (100 or 200 cc) over the trough, and carry the filled cylinder to a flame—the gas will explode. Let the Kipp be emptied a few times, filling up by closing the stop-cock. Trying another cylinder of the gas now collected, it will burn quietly, without explosion; this is a sign that the gas is free from air.

4. THE EXTREME LIGHTNESS of the inflammable air is shown by holding a cylinder containing air for a few moments over a cylinder containing the gas, and now trying both at the flame, the gas in both will burn with explosion.

Careful determinations have shown that under ordinary conditions (of temperature and pressure) twelve cubic centimeters of inflammable air weigh one milligramme (0.083 mgr. per cc).

5. The gas generated from zinc has not as unpleasant an odor as that generated from iron; it is less impure. TO PURIFY A GAS it must pass slowly through absorption and washing tubes, containing the proper absorbents. If these are in the liquid form, it requires pressure to force the gas through; hence, it is generally preferable to soak fragments of pumice with the absorbent liquids and pack these fragments in cylinders.

6. The most effective ABSORBENTS for purifying inflammable air are lead and silver solutions (removing the odorous gases), caustic potash solution (removing traces of acids) and concentrated oil of vitriol one of the most effective dryers, being strongly hygroscopic.

7. For such purposes the Drechslers are not applicable. We generally use cylinders of glass, on foot, so they will stand firmly, and provided with a tubulature in a lower division, separated from the main upper parts by a narrow contraction, preventing the fragments of pumice from falling. Connection is made by rubber stopper and glass tubing at the top opening and at the tubulature below. A number of such cylinders are used in series.

8. If the inflammable air is carefully dried so that it will pass through a tube surrounded with fragments of ice without depositing moisture in the same, it can be connected with a small burner (like the microchemical burners) and, after due precautions, the jet may be lit. IT WILL BURN with a pale, very hot flame. A bell glass held over the flame will bedew, and WATER will soon run in drops down into a plate placed to receive it.

9. Since inflammable gas produces or generates water (Greek: *hydor*) when burning, it was called HYDROGEN by Lavoisier (p. 19). The chemical symbol of hydrogen is H.

Experience has shown that HYDROGEN IS CLOSELY RELATED TO THE METALS, several of which form genuine alloys with it. Palladium absorbs a thousand times its own

volume of hydrogen (Graham); it is used in gas analysis to remove hydrogen from other gases.

10. In recent days, since very low temperatures have been produced on a sufficiently large scale, it has been found (Olszewski, 1895) that the CRITICAL POINT of hydrogen gas is at 234.5 degrees below the freezing point, and that the critical pressure is 20 atmospheres. Below this temperature hydrogen is a vapor, liquefiable by an increase of pressure.

11. Any of the acids can be used instead of muriatic, especially nitric, sulphuric and even acetic. THE METALS THAT DISSOLVE more or less readily IN some of these DILUTE ACIDS are, in addition to iron and zinc: Magnesium, aluminium, cadmium, nickel, cobalt, lead. The special conditions of solution will be studied in due season. Lead is insoluble in both muriatic and sulphuric acids.

12. In many cases, especially where sulphuric acid has been used, CRYSTALS FORM, in which the blowpipe readily detects the metal originally dissolved. Some of these crystals, especially the sulphates, contain water of crystallization, easily driven off by heating the crystals in a glass tube.

## 18. SUBSTITUTION BY SOLUTION.

1. THE CONTRAST between the solution of marble and metals in ACIDS and salts in WATER must have become apparent. When the salt dissolves in water nothing escapes, and upon evaporation, the original salt is reproduced, frequently in crystals. When the metals dissolve in acid, a gas escapes, a new substance forms, no longer the metal, but containing the metal, as proved by means of the blow-pipe.

2. Accordingly we have two different kinds of solution, simple and CHEMICAL SOLUTION, also distinguished as solution and dissolution. The first is largely physical in its nature; the second is entirely chemical, the original sub-

stances both disappear and are replaced by two new and totally different substances. Thus we have entered the very center of CHEMISTRY IN THE WET WAY.

3. In the solution of any metal in a dilute acid, HYDROGEN GAS is always produced. The solution obtained in many cases—detailed directions belong to practical chemistry—crystallizes, in all cases can be evaporated to dryness, so that the new salt is obtained by itself, free from water and any excess of acid—the last best avoided by having an excess of metal, and decanting the solution. IN THE SALT, the blowpipe readily detects THE METAL used and dissolved.

4. For example, in the preparation of hydrogen gas by means of zinc and dilute sulphuric acid, we obtain the gas and a white crystallized salt containing zinc; this salt is identical with common white vitriol. A solution of this salt gives an abundant white precipitate with lead acetate, precisely as does the acid used; it contains, therefore, the essential or chemical characteristic part of sulphuric acid. Hence, it is termed a sulphate, namely ZINC SULPHATE.

5. The chemical solution considered may now be represented thus: Zinc and sulphuric acid give hydrogen gas and zinc sulphate. Evidently the hydrogen must have formed part of the sulphuric acid. It is known to be metallic in its real nature (17.9). We have here apparently an exchange of metals, hydrogen for zinc; consequently the acid itself must be hydrogen sulphate. In other words, the ACID IS A HYDROGEN SALT, exactly as white vitriol is a zinc salt, the salt of a metal.

6. The above REACTION—that is chemical action—between the metal and the acid may therefore be written as follows: Zinc and hydrogen sulphate give hydrogen and zinc sulphate. Such a reaction in which any substance A takes the place of any other substance B in any combination, setting free this second B, is called a SUBSTITUTION. The above reaction is the substitution of zinc for the hydrogen of the acid. See blackboard diagram.



7. Having studied the qualitative side of this fundamental reaction, we must next try to determine the QUANTITATIVE RELATIONS of the same. The merest trials show that without weighing the quantities used, there either remains metal or acid in excess. To obtain the best salt it is generally advisable to have an excess of the metal, decanting the liquid when the reaction ceases and setting the liquid aside to crystallize.

8. First, TO DETERMINE THE AMOUNT OF HYDROGEN GAS the latter must be measured in a gas burette. The evolution tube is charged with an excess of the acid and the accurately weighed metal—the latter held on the slanting walls of the dry, inclined tube above the acid. When the burette is properly adjusted, the operation is started by simply bringing the evolution tube to a perpendicular.

9. MAGNESIUM ribbon is specially convenient for these determinations. It is found that a cubic centimeter of hydrogen gas is produced for each milligramme of magnesium used, very nearly. As 12 cc hydrogen gas weigh one milligramme (17.4) THE UNIT OF ONE MILLIGRAMME OF HYDROGEN IS EQUIVALENT TO TWELVE MILLIGRAMMES OF MAGNESIUM.

10. Repeating the experiment with zinc we find that it requires nearly 32 mgr. of zinc to give 12 cc gas representing 1 mgr gas, at the same time (under same pressure and temperature). For iron the equivalent number is 28. For aluminium—easiest dissolved in an alkaline liquid (13.5)—the equivalent is found to be 9. Accordingly 1 of hydrogen (by weight) is equivalent to 9 Al, 12 Mg, 28 Fe, 32 Zn (really 31.75). These numbers are called the CHEMICAL EQUIVALENTS of the metals.

11. Careful experiments, on a small scale with accurate weighings, show that PER UNIT of weight of metal dissolved in sulphuric acid, THE CRYSTALLIZED SULPHATES WEIGH: For Mg, 10.25; Fe, 4.96; Zn, 4.38; Cd, 2.49. If carefully heated to drive out the water of crystalization, the residual

anhydrous sulphates weigh respectively 5.00, 2.71, 2.46 and 1.85 times as much as the metal used. Lead converted into nitrate weighs 1.60, into crystalized acetate (sugar of lead) 1.83 per unit.

12. Careful experiments of this kind also permit the determination of the CHEMICAL EQUIVALENTS OF THE ACIDS themselves. Thus, since 1 Mg gives 5.00 dry sulphate, the equivalent 12 Mg gives 60 Mg Sate, in which the non-metallic matter (the Sate) is  $60-12=48$ . But the acid contains  $H=1$  as metal or instead of the metal. Hence, the chemical equivalent of sulphuric acid,  $H\ Sate$ , is 49. In a like manner, the equivalent of nitric acid is found to be 63, and that of muriatic acid, 36.5.

## 19. SOLUTION OF SILVER AND GOLD.

1. Dilute sulphuric or muriatic acids have no effect whatever on copper, mercury and silver, nor on gold and platinum. All these metals are insoluble in dilute acids. But when heated with CONCENTRATED sulphuric ACID, the first three dissolve, yielding a noxious gas having the odor of burning sulphur; the last two, gold and platinum, remain insoluble even in boiling concentrated sulphuric acid.

2. Very dilute nitric acid, in the cold, has but little action on the first three metals (Cu, Hg, Ag), but when the acid is reasonably strong—say 10 per cent.—it acts quite promptly, especially when moderately heated. While the metals dissolve, a very noxious reddish gas (RUTILANT VAPORS) is produced in abundance.

3. The rutilant vapors invariably make their appearance when strong nitric acid exerts its dissolving influence. When a filter paper or sponge with aqua ammonia is brought near, ABUNDANT WHITE CLOUDS take the place of the noxious vapors, which evidently combine with the ammonia to a white solid. In this way, the solution may be effected in a room not provided with hood.

4. Nitric acid (AQUA FORTIS), even when boiled, has no effect on gold nor on platinum; they are insoluble in all ordinary single acids. In fact, gold is generally separated from its alloy with silver, by boiling the alloy with concentrated sulphuric acid or with nitric acid under conditions established by long practice; the amount of gold present must be less than one-fourth in the alloy. This accounts for the common name of nitric acid in german: Scheide wasser. Compare this wet way process with the dry way separation, 8, 12.

5. AQUA REGIA (4 muriatic with 1 nitric acid) dissolves gold (foil) readily. Both gold and platinum are dissolved by moderately heating them with this acid in large excess. When all metal dissolved, the excess of acid is driven off, carefully avoiding overheating, as that would decompose the MURIATE obtained (test, 13, 10). Dissolving in water, we have the common solutions of these two metals; muriate of gold and of platinum.

6. The nitrates of copper, mercury and silver are readily obtained in crystal form. Silver nitrate crystallizes generally in rhombic tablets, of almost 130 degrees. Silver and its salts are very sensitive to light and to many gases, and even to dust, so that good, colorless (or white) crystals can only be obtained under specially favorable conditions.

7. The nitrate of mercury obtained varies with the conditions under which the metal is dissolved. When at common temperature, acted upon by dilute nitric acid, the resulting nitrate is precipitated abundantly by the muriatic acid or by salt; it is called MERCUROUS NITRATE. When the metal is acted upon by reasonably strong acid on the water bath, the resulting nitrate is not precipitated by muriatic acid or salt; it is called MERCURIC NITRATE.

8. The sulphates of mercury show the same difference. Heating the metal with less than half its weight of concentrated sulphuric acid gives MERCUROUS sulphate; while heating mercury with twice its weight of concentrated acid until the excess of acid is driven off, gives MERCURIC sul-

phate. The distinction is made as before stated; the mercurous solutions are precipitated by muriates. The precipitate is CALOMEL; the other muriate is SUBLIMATE.

9. When trying to dissolve the mercuric sulphate, an abundant yellow precipitate—the TURPETH MINERAL—forms, a so-called basic sulphate, while the balance or acid sulphate passes into solution. By adding about 5 per cent (sulphuric) acid to the water, the entire salt will be dissolved, and no yellow precipitate will form. When it has formed, such addition of acid will redissolve it.

10. If the residue from copper and concentrated acid is taken up in warm water, the resulting solution will deposit the crystals of blue vitriol described (15.9).

In this manner ALL METALS HAVE BEEN BROUGHT INTO SOLUTION, excepting the modern light metals potassium and sodium (6.12). Greenish iron solutions in presence of nitric acid become reddish; these are called FERRIC, the original greenish FERROUS.

11. THESE SOFT METALS have to be kept in well stoppered bottles under pure naphta, and even then their surface soon looks dull and corroded. When freshly cut with a knife the surface looks brilliant white like silver. Thrown on water the metal floats, melts (round globule) and burns with a purple (Ka) flame, finally exploding; hence, the experiment must be made in a deep beaker with but an inch of water. Sodium is less violent; burns with yellow flame.

12. The solution so obtained is strongly alkaline. Evaporated to dryness and fused, the CAUSTIC ALKALIES are obtained. Made carefully in a large nickel crucible, the experiment yields 1.74 of caustic soda, 1.43 of caustic potassa per unit of metal.

It may also be added that a UNIT WEIGHT OF METAL GIVES 1.44 Ag Sate, 1.57 Ag Nate, 1.60 Pb Nate, 3.94 blue vitriol, 1.48 mercuric sulphate; 1.24 mercurous sulphate; 1.18 calomel and 1.35 sublimate. Accordingly, the EQUIVALENT of SILVER is about 108, of lead 104. See 18, 12.

## 20. REDUCTION IN THE WET WAY.

1. THE FOUR SOLVENTS used for the solution of the metals are water, dilute acids, concentrated (single) acids and aqua regia. The type metals, soluble in these solvents, are POTASSIUM, ZINC, SILVER and GOLD. To the most soluble group belong Ka, Na, as shown; also Ca, Sr, Ba. Insoluble in water, soluble in dilute acid are: Mg, Al, Zn, Fe, Pb. Requiring a concentrated acid are: Cu, Hg, Ag. Requiring aqua regia: Au, Pt.

2. In each of the four groups, the metals have been enumerated according to their DEGREE OF SOLUBILITY. Thus, experience shows that Mg is clearly the most soluble, Pb the least soluble, of those mentioned in the second group; also Zn more soluble than Fe, but less soluble than Al and Mg.

3. But if into a blue copper solution a piece of iron be thrown, the iron will become covered with red copper and the solution will lose its fine blue color, soon appearing colorless; if exposed for hours to the air, the iron now in the solution will show a rust-like precipitate. Evidently, the more soluble iron has taken the place of the less soluble copper in the solution. We have a substitution of iron for copper.

4. This rule is general. A MORE SOLUBLE METAL WILL TAKE THE PLACE OF ANY LESS SOLUBLE METAL IN A SOLUTION. A gold solution will deposit its gold upon a piece of metallic silver and be changed to a silver solution. This silver solution will surrender to mercury, a mercury solution to copper, the latter to lead, the lead solution to zinc.

5. THIS REDUCTION OF THE METALS IN THE WET WAY finds important applications in the arts as well as in the laboratory. Copper-waters issuing in mining regions are run into large reservoirs, and old iron thrown in; after some weeks this iron seems to have been converted into copper. (Hungary).

6. In the laboratories, the most elegant and conclusive TEST FOR METALS IN THE WET WAY is this very reduction by substitution. A drop of the solution to be tested is placed on a microscope slide, and a minute clipping of a more soluble metal (generally zinc) placed in that drop. Almost instantly the substitution takes place, beautiful crystals of the metal in solution growing as it were out from the zinc, forming elegant groupings.

7. Even the alchemists were familiar with these reactions, though some are believed to have considered these simple substitutions evidences of transmutation of copper into silver, of zinc into lead. A dilute lead solution with brass wires and a fragment of zinc, gives the old arbor saturni (LEAD TREE) brilliant crystals of pure lead coating the wires like leaves and branches on a tree. A silver solution with mercury gives arbor dianæ, the SILVER TREE, growing up from the mercury.

8. By putting a weighed amount of the more soluble metal into an excess of a solution of the less soluble metal, an EQUIVALENT amount of the latter will be precipitated and can be weighed after proper separation and drying. However, for several pairs of metals it is difficult to get accurate results, the metals changing too readily.

9. It is found that the silver precipitated weighs exactly nine times as much as the magnesium used; hence the chemical equivalent of silver is 9 times 12 or 108. For every unit of copper thrown into a silver solution, 3.39 units of the latter are obtained from its nitrate solution, especially if the solution is kept in a cool place. The equivalent of copper, therefore is 108, divided by this number, or about 31.6. Silver thrown into a gold solution gives the equivalent of gold about 66.

10. THE CAUSE of these substitutions is given by the facts of solubility of the several metals taken singly. Thus, copper does not dissolve in dilute sulphuric, while zinc does

so readily. If copper and zinc together are thrown into the same dilute acid, the zinc will dissolve, the copper not. There can be no question about these facts. Surely, zinc is much more soluble than copper.

11. Now if metallic zinc be thrown into a solution of blue vitriol, we have THE SAME THREE BODIES—zinc, copper and the dilute acid—in the same dish and the same final result ought to be obtained, a zinc solution with metallic copper. Such is actually the case; zinc displaces the copper from its solution because zinc is much more soluble than copper.

12. The common talk about CHEMICAL AFFINITIES of these metals is nothing but reasoning in a circle, and the attempt to hide this false reasoning by the introduction of the high sounding term. If zinc has greater affinity for the acids than the copper, nobody knows of that except by the very experiment which it was attempted to explain.

## 21. SULPHUR AND SULPHIDES.

1. SULPHUR was known to the ancients. Already, Homer speaks of the purifying effects of burning sulphur (fumigation). Its faint blue flame imparts pallor to the face in the dark. Hence, the ancients burnt sulphur at certain religious ceremonies.

2. THE OLD CHEMISTS detected sulphur in many ores which upon heating in the open fire, emit the odor of burning sulphur abundantly (9. 3). These ores generally having metallic luster, the ancients smelting metals from them, concluded that sulphur is a constituent of metals themselves. To change baser metals to gold seemed to the alchemist to involve simply a removal of sulphur or something like sulphur.

3. SULPHUR continues to be a most important substance to CHEMICAL INDUSTRY. About 400,000 tons. worth 10



million dollars, of native sulphur are produced yearly in Sicily alone, where 25,000 laborers dig for it.

For many purposes the sulphur of ores is also available. Pyrites contain about 50 per cent. of sulphur, and occur in immense deposits (9. 8).

4. NATIVE SULPHUR is a yellow solid, hardness and gravity very near 2. Its luster is peculiar, resinous. It is a very poor conductor for heat and electricity, and very brittle. Fine specimens (crystals) are transparent. It is readily fusible (113 degrees), and on boiling (about 450 degrees) forms a brownish red vapor, which condensed gives flowers of sulphur as sublimate. Melted sulphur, cast in forms, gives roll-sulphur. At about 200 degrees melted sulphur becomes viscid; above that temperature, it gets limpid again.

5. Sulphur when absolutely pure has no odor, not being volatile at common temperatures. When heated in the open vessel, it burns with a pale blue flame (250 degrees) far below its boiling point; the gas produced is suffocating, of the familiar and characteristic odor of burning sulphur.

Sulphur is not soluble in water, but quite soluble in essential oils, from which it crystallizes in the forms exhibited by native sulphur.

6. NATIVE SULPHUR CRYSTALS from Sicily (see p. 69) are very beautiful and often quite large. They are (stable or permanent) rhombic octahedra;  $OO'$  106.6; sharp edge 85.0; lateral  $OO''$  143.3. Quite generally the sharp corners are truncated by the base P, forming PO 108.4. The sharp edge CB is also frequently truncated by the face q, for which Pq 117.8, Oq 132.5 and mutually over middle edge,  $qq'$  124.4. Finally the edges PO are often truncated by an obtuse octahedron o, for which Po 134.5. The basal rhomb has 101.8. These faces are readily identified even on small crystals from solution.

7. MELTED SULPHUR CRYSTALLIZES (p. 69) upon cooling, forming (unstable) nearly square prisms  $MM'$  90.6, cut off

obliquely by the base P, so that Pa 95.8, the face a replacing the edge MM'. The lateral corners are often replaced by the triangular faces q, while PM may be truncated by the octahedral o. Characteristic angles are MP 94.1; Ma 135.3. Pq 135.1; qq' over P 90.3. These dimensions are easily identified. Showing two different crystal forms, sulphur is said to be DIMORPHOUS.

8. SULPHUR melted or as vapor COMBINES WITH many METALS to new bodies, called SULPHIDES. Several of these artificial sulphides are identic with native sulphides. Copper—in foil or turnings—when reached by the vapor of boiling sulphur, burns brightly. The malleable copper used is thus converted into a very brittle blueish black sulphide.

9. Mercury, silver, iron, lead, zine and most other ordinary metals combine in a like manner with sulphur. The coarsely divided metals (filings, turnings, thin foil, etc.) need only be melted with sulphur in a crucible.

Melting together equal weights of iron and sulphur gives the BLACK IRON SULPHIDE, very much used in chemical laboratories; it is distinguished as FERROUS SULPHIDE from the native yellow iron sulphide, pyrite (9, 8). Iron filings mixed with flowers of sulphur, and moistened, also give ferrous sulphide—the mixture may even inflame (Lemery's Volcano).

10. DUMAS (portrait p. 25) exposed pure silver foil in a combustion tube to the vapors of sulphur, and obtained finely crystallized silver sulphide. He found 1.148 of sulphide per unit of silver used. The increase of 14.8 per cent. of silver (equivalent 108) gives 16 as the chemical EQUIVALENT OF SULPHUR.

11. If fragments of charcoal are heated in a combustion tube while vapors of sulphur are passed over them, a very volatile, highly inflammable liquid is formed, which will condense in a cooled receiver. It is called CARBON BISULPHIDE, and is the best solvent for sulphur, taking up nearly half its

weight at common temperatures. From this solution, splendid sulphur crystals can be obtained.

12. GUN POWDER IS A MIXTURE of sulphur, carbon and nitre in the proportion 1: 1: 6. Washing with water removes the nitre, the identity of which will be revealed by its prismatic crystal form, (15, 10). The well dried residue yields sulphur to the bisulphide, from which fine crystals readily deposit, showing the octahedron O, the base P, and frequently the truncature q, all readily identified by the figures given, using a magnifier. Insoluble, black carbon finally remains. Thus the gun powder was ANALYZED, separated into its constituent parts.

## 22. HYDROGEN SULPHIDE AND METALS.

1. Ferrous sulphide (21.9) covered with almost any diluted acid, gives strong effervescence, both in bulk of gas produced and in odor. The latter is that of rotten eggs. This reaction or chemical process is readily understood. The acid, say H Muriate with Ferrous Sulphide gives HYDROGEN SULPHIDE GAS and Ferrous Muriate remains in the green solution. Rouelle first noticed this gas, which Scheele soon after studied thoroughly.

2. In this reaction, the substances taken, H Mrate and Feous Side, yielding Feous Mrate and H Side gas, have evidently interchanged their constituents. They are said to have undergone DOUBLE DECOMPOSITION—in this case by VOLATILIZATION, the product being a gas. Such reactions are very common in chemistry.

3. HYDROGEN SULPHIDE GAS is quite soluble in water, to which it imparts a strong and highly characteristic odor. When left exposed to the air, such sulphuretted water soon becomes opalescent, and gradually a white deposit forms—this is finely divided sulphur (white streak, substance yellow). Some springs produce such sulphuretted water in abundance, and are very valuable medicinally.

4. Silver coin and ware, especially when moist, turns black when exposed to the gas or the water; lead paint and compounds of lead, bismuth, silver and other metals, also turn promptly brown or black. Accordingly, hydrogen sulphide is a most IMPORTANT REAGENT by means of which heavy metals can be recognized. During working hours, the chemical laboratories keep this gas on tap in a large Kipp generator for constant use.

5. A lead solution of ordinary working strength—say one per cent—is perfectly colorless and transparent. A few bubbles of the hydrogen sulphide gas passed into it almost instantly blackens it, forming an abundant black precipitate of  $PbS$ , settling soon to the bottom. Even when extremely dilute, a brownish coloration will be produced in lead solution by  $H_2S$  gas. This gas is the most sensitive reagent known for lead in solution. For this reason, lead solutions are replaced by barium solution as reagent for sulphates (13, 12).

6. The black lead sulphide PRECIPITATE being solid, may be readily separated from the liquid by FILTRATION, and by WASHING, best adding a little hydrogen sulphide to the wash water; drying then removes both water and excess of hydrogen sulphide.

This precipitate is not only insoluble in water but also insoluble in dilute acids (nitric, acetic must be tried for sulphuric and muriatic produce precipitates themselves, 13.8).

7. This reaction evidently again is a double decomposition, for both substances taken interchange constituents. The lead acetate and hydrogen sulphide gas give lead sulphide and hydrogen acetate (acetic acid). But it differs from the preceding case (2) by the product being an insoluble instead of a volatile compound. The present reaction is therefore a DOUBLE DECOMPOSITION BY PRECIPITATION.

8. It is evident that all SULPHIDES INSOLUBLE IN DILUTE ACID will precipitate by sulphide gas in acidified solutions. The corresponding metals which thus may be

precipitated as sulphides are, in proper groupings: a) Ag Hg<sup>ous</sup>, Pb; b, Cu, Hg<sup>ic</sup>, Cd, Bi; c) As, Sb, Sn; d) Au, Pt. They are distinguished a) by precipitate with muriates (their muriates insoluble); c and d, the sulphide precipitates soluble in yellow Am Side. Solution of c colorless, d yellowish.

9. YELLOW AMMONIUM SULPHIDE is obtained by saturating aqua ammonia with hydrogen sulphide gas, and perhaps dissolving some flowers of sulphur in it. The precipitate is tested while still on the filter, but completely washed with water, so that the washing is entirely free from acid reaction (a drop making no red stain on blue test paper). If the acid were not completely removed, it would decompose the reagent, giving hydrogen sulphide gas and an abundant precipitate of sulphur.

10. The other heavy metals (not precipitated by hydrogen sulphide gas because their sulphides are soluble in dilute acids) do come down when the solution is made ALKALINE by a reasonable excess of ammonium hydrate (sufficient to give the odor). These metals are f) Zn, Mn, Fe<sup>ous</sup>, Ni, Co and g) Al, Fe<sup>ic</sup>, Cr<sup>ic</sup>. In case of Ferric, the hydrogen sulphide first makes the solution opalescent (from separation of S) and ferrous, then precipitates this black.

11. The two groups f and g are readily distinguished by the latter giving a precipitate by ammonium hydrate after the solution has been treated with an excess (as solvent) of ammonium muriate, while the metals grouped under f do not give a precipitate under these conditions i. e. their HYDRATE is SOLUBLE IN SAL AMMONIAC (or ammonium muriate).

12. THE LIGHT METALS, Ka, Na and Mg, Ca are not precipitated by hydrogen sulphide gas under any conditions, their sulphides being soluble in water. Thus, the metals in solution are almost as readily distinguished by means of hydrogen sulphide gas and a few other reagents as by the blowpipe in the dry way. We shall soon return to this most important subject of CHEMICAL ANALYSIS IN THE WET WAY.

NOTE.—The following preliminary tabular exposition of the COURSE IN WET WAY ANALYSIS FOR METALS comprises only the general reactions determining the groups, and the special features which in these reactions mark the individual members. These are the only reactions sufficiently explained in the preceding. Only one metal is here supposed to be in the solution, which thus contains a simple compound only and is not complex.

1. Solution + H Mrate — white precipitate—SILVER GROUP I. Precipitate soluble in much water, Pb; precipitate soluble in Am H<sub>2</sub>ate, Ag; insol., turning black, Hg<sub>2</sub>ous.
2. Solution + H S<sub>2</sub>ate, white precipitate, BARIUM GROUP, II. Very dilute solution, no precipitate, Ca; a precipitate forms promptly, Ba, very slowly, Sr. If solution black by H S<sub>2</sub>ide, it contains Pb, from I.
3. Acidified (mur) solution, saturated with H S<sub>2</sub>ide gas gives a precipitate (other than merely S) . . III, IV, V. The precipitate washed and treated with yellow Am S<sub>2</sub>ide remains insoluble, III; or dissolves IV, V.

III. COPPER GROUP. Original solution blue or green . . Cu. Precipitate first whitish, then yellowish, brownish, finally black . . Hg<sub>2</sub>ic; precipitate yellow . . Cd; brown . . Bi. Precipitate soluble in yellow Am S<sub>2</sub>ide; original solution colorless, . . IV; yellow to brownish . . V.

IV. ARSENIC GROUP.—Color of sulphide precipitate yellow, . As; orange . . Sb; brownish . . Sn.

V. GOLD GROUP.—Original solution precipitated brownish by ferrous solution . . Au; yellow by sal ammoniac solution . . Pt.

4. Solution (3) made alkaline with ammonia after adding considerable Am Mrate; a precipitate forms VI or VII.

Original solution with excess sal ammoniac, made strongly alkaline with Am H<sub>2</sub>ate, no precipitate, VI; a precipitate VII.

VI. ZINC GROUP. Original solution, deep green, Ni; pink, Co; pale rose, Mn; pale green, turning rusty, Fe<sub>2</sub>ous; colorless, Zn.

Am S<sub>2</sub>ide precipitate=white, Zn; flesh colored, Mn; black, Fe<sub>2</sub>ous, Ni, Co, distinguished by color of original solution (or dry way borax bead, 6, 11).

VII. ALUMINIUM GROUP. Original solution, colorless, Al; green, Cr; yellow to orange, Fe<sub>2</sub>ic. The precipitates have nearly the same colors.

5. If no precipitate obtained: Magnesium group, VIII. Solution with much sal ammoniac, made strongly alkaline with Am H<sub>2</sub>ate; to portions of this mixture, add
  - a) Am Cate; a precipitate forms, or at least on adding Am Oxalate . . Ca from II.
  - b) Na Pate, white crystalline precipitate . . Mg.

Original solution or substance, with  $\text{K}_2\text{Hte}$ , odor of ammonia; red paper turned blue . . Am.

Flame coloration, persistent and intense yellow . . . Na, purplish, and through blue glass deep reddish . . . Ka.

It is understood that the tests are carried on till the substance is found, not beyond (for simple solutions), throughout this course. Thus, if found in reaction 1, none of the others is tried; if in 5, reaction gives a precipitate, that ends it. For diagram of this course see p. 73.

## 23. IODINE AND IODIDES.

1. Iodine is a solid substance which in many respects resembles sulphur, especially in its action on metals. While now in the market of chemicals because of its many applications, it was not known till 1811, when COURTOIS discovered it in ashes from sea weeds. It is mainly obtained from the mother liquors of Chili saltpeter.

2. IODINE is a grayish black solid, sufficiently volatile to make its offensive and characteristic odor perceptible at common temperatures. Its main properties are: G 4.50, F 113 and B 180 degrees. Its vapors have a beautiful deep violet (Greek: *iodos*) color; hence its name and chemical symbol  $\text{I}_2$ . It is sufficiently soluble in water to tinge it yellow. It is more soluble in alcohol, and abundantly soluble in chloroform and carbon bisulphide.

3. Both from solution and by sublimation it crystallizes quite readily. On account of its marked volatility, IODINE CRYSTALS are not permanent, but disappear and form again in the containing vessels, according to the changes in temperature. The crystals are rhombic tablets. Compared to the sulphur crystals (p. 69) the angles are  $\text{OO}''$  136 and  $\text{PO}$  112 degrees.

4. STARCH PASTE is colored deep blue by iodine; the color disappears on heating to about the boiling of water, but promptly re-appears on cooling. This reaction is one of the most delicate or sensitive we have in the wet way. The merest trace of iodine in solution can be revealed by this TEST. One part of iodine in a million of solution will show



the color with starch paste; in 10 cc of such a solution there is the hundredth part of a milligram of iodine.

5. Passing hydrogen sulphide gas through a solution of iodine in chloroform or bisulphide under water, the intense red color will gradually disappear and the water will become turbid from sulphur. This is evidently a substitution of iodine for sulphur.  $I_2$  and  $H_2S$  giving  $S$  and  $HI$ . Decant, filter and by gentle heating drive off the excess of  $H_2S$ , and a strong solution  $HI$  or HYDRIODIC ACID remains. This colorless solution gradually decomposes, setting free iodine, as indicated by the yellow color it assumes.

6. Finely pulverized metallic arsenic thrown into a solution of iodine in bisulphide, combines with the iodine, forming ARSENIC IODIDE, which separates in brick red, brilliant, thin tablets upon the volatilization of the solvent. This  $AsI_3$  is readily fusible and volatile; it sublimes without decomposition (Synthesis).

7. Iodine, like sulphur, unites with most metals in the dry way. Heating a glass vessel containing a little mercury, this will deposit, by distillation, in small metallic globules on the inner walls of the vessel. When this has cooled again, heat an equal weight of iodine in the same; as the violet vapors reach the mercury, they combine therewith, forming crystals of MERCURIC IODIDE.

8. Mercuric iodide can be readily moved from one place to another by heat; it will deposit by sublimation on the colder parts of the vessel. At first it forms YELLOW prismatic crystals of 114.5 degress. Gradually it turns BRILLIANT RED; this change may be produced instantly by rubbing the yellow crystals with any hard body (a glass rod). The red crystals are generally tabular, with a pyramid inclined under 109.5 degrees to the base; hence quadratic (10.3). Mercuric iodide is DIMORPHOUS (21, V).

9. THE SMALLEST TRACE OF MERCURY may be positively IDENTIFIED in the dry way by applying these reactions

in a small blowpipe test tube of hard glass, and observing the results with a magnifier and under the microscope. The metal is identified by the distillate consisting of minute white globules, having brilliant metallic luster. The iodide is next formed by synthesis, its colors and crystal forms recognized. This series of tests is important in toxicology.

10. Iron, in the presence of water, combines readily with iodine, forming FERROUS IODIDE, which being freely soluble in water, is purified by simple filtration. See 21.9.

With potassium carbonate,  $K_2CO_3$ , there will form a precipitate containing the iron (as shown by blowpipe) and from the filtrate, permanent CUBICAL CRYSTALS of potassium iodide are obtained.  $Fe^{ous} I_{ide}$  and  $K_2CO_3$  give  $Fe^{ous} CO_3$  (insol) and  $K_2I_{ide}$  (sol). By synthesis, the iron takes the iodine, and by double decomposition this is transferred to the potassium.

11. Potassium iodide is the most important soluble iodide; by its means the INSOLUBLE IODIDES are readily obtained as PRECIPITATES from the solution of the metals. Thus  $Pb I_{ide}$ , yellow; hexagonal tablets readily crystallize from solution in hot water.  $Hg^{ic} I_{ide}$  red; first pink, then rose, finally brilliant red; soluble in excess of reagent,  $K_2I_{ide}$  to colorless solution. Mercurous solutions give dirty green  $Hg^{ous} I_{ide}$  as precipitate.  $Ag I_{ide}$  is yellowish white, insoluble in ammonia (distinction from muriate).  $Bi I_{ide}$  is brown. All other iodides are soluble, hence not obtainable by precipitation.

12. NITRO-NITRIC ACID (concentrated nitric acid saturated with rutilant vapors, 19.2) instantly SETS FREE THE IODINE OF IODIDES; the free iodine may be recognized by its color, solubility in chloroform and the starch reaction, 4. Shaking the solution with chloroform, the free iodine will collect in this solvent, tinging it deep red, while the aqueous solution becomes colorless. Now making the solution alkaline, the iodide is reproduced, and the chloroform loses its color. Such operations with NON-MISCIBLE SOLVENTS (as water and chloroform) are very important, especially in toxicology.

## 24. ACIDIMETRY AND ALKALIMETRY.

1. Vinegar and lime are the oldest representatives of two important classes of substances endowed with opposite characters; namely ACIDS AND BASES (13). Muriatic, nitric and sulphuric acids correspond to the first; the caustic alkalies to the second. Stronger solutions of these substances are corrosive; when exceedingly diluted, the former taste sour (acid), the latter not. Add the strong acid to the water while stirring, when diluting.

2. But certain coloring materials are most sensitive INDICATORS of the presence of either of these bodies, so that the dangerous method of tasting never is resorted to by chemists. The most common indicators are litmus, cochineal and phenolphthalein. A drop of these solutions show even with exceeding dilute solutions of acid or base: litmus, red and blue; cochineal, orange and purplish red; phthalein, colorless and deep red.

3. Pure water, alcohol and kindred liquids do not change the color of these indicators. Such liquids are said to be neutral, or to have a neutral reaction. The extreme sensitiveness of the indicators or the extraordinary DELICACY OF THE REACTION may be shown by adding a single drop of dilute alkali solution to half a beaker full of water tinted ruby red by a drop of cochineal tincture; on stirring it turns instantly purplish red. A drop of an equivalent acid solution turns it ruby red, the next turns it orange.

4. THESE CHANGES CAN BE REPEATED an indefinite number of times, most conveniently by having acid and base in two BURETTES. The liquid must be well mixed after the addition of each drop, best by giving a circular motion to the beaker glass. The change will be sudden upon the addition of a single drop; really half of this drop saturates the remaining acid, the other half causes the final change in color or reaction.

5. In this manner THE RELATIVE STRENGTH or chemical equivalents of given solutions of acid and bases are readily DETERMINED. Suppose that 5 cc of an acid solution, with water and phthalein, shows no change upon the addition of 7.8 cc of alkali, but at 7.85 suddenly turns red; then 7.85 cc of this alkali are equivalent to 5 cc of the acid. This alkali solution is accordingly 1.57 times as strong as that acid.

6. If now the strength of the acid be known, that of the alkali will have become determined by the operation. In VOLUMETRIC CHEMICAL ANALYSIS the unit of the strength of solutions is NORMAL (N), and CONTAINS ONE MILLI-GRAMME-EQUIVALENT PER CUBIC CENTIMETER. If the acid used above was normal, then the alkali found is 1.5 N. The equivalent of sodium hydrate being 40 (as we soon shall learn), it would contain 1.57 times 40 or 62.8 mgr. per cc in the above instance. This is ALKALIMETRY.

7. The unit of the chemical equivalent being hydrogen (18, 9, 10) the strength of the acid is established by MEASURING THE HYDROGEN GAS evolved from a measured volume of the acid acting upon an excess of magnesium ribbon. Thus, suppose that 5 cc of the dilute acid had been taken, and 75 cc hydrogen gas had been obtained, while a considerable amount of magnesium remained undissolved; then 1 cc acid gave 15 cc gas or the acid is 1.25 N. This is ACIDIMETRY.

8. If a number of careful determinations concordantly give that result (1.25 N), a stock of NORMAL ACID will be obtained by diluting 100 cc to 125 or adding to a liter of the acid a quarter liter of water. Since the equivalent of sulphuric acid is 49 (18.12), the normal acid, if sulphuric, contains 49 mgr of acid per cubic centimeter; if nitric, 63 mgr; if muriatic. 36.5 mgr.

9. Having thus obtained a stock of normal acid, it is easy to prepare a corresponding stock of NORMAL ALKALI (see 6). With these normal solutions the unknown strength of acids and bases is determined in the manner indicated. As a

matter of fact, the specific gravity of normal hydrates (K<sub>a</sub> or Na) is about 1.044, of sulphuric and nitric acids about 1.032 and muriatic about 1.016. Hence, if solutions run from 1.05 to 1.10 they are suitable for making normal solutions.

10. Not one of these alkalis or acids is obtainable in the free state in exactly weighable condition; hence, the preceding method of standardizing by means of an accurately weighed metal is necessary. It has, however, been found, that pure and CRYSTALLIZED OXALIC ACID is permanent in air, when kept in well stoppered bottles. Numerous and careful experiments have shown its equivalent to be 63. By evaporating a normal solution of pure caustic alkali in a silver dish and fusing the residue, the equivalent of caustic soda is found to be 40, that of caustic potassa 56, approximately.

11. Hence, 63 mgr of crystallized oxalic acid, represents 1 cc normal acid. TO TEST ANY ALKALI SOLUTION, it is only necessary to weigh off as accurately as possible, say 630 mgr of such crystallized oxalic acid, transfer to beaker, add water and indicator (best phthalein); this represents 10 cc N. If now the alkali is run in—first rapidly, then drop by drop—and suddenly turns the liquid permanently red when 9.85 have been used, it is not exactly normal, but 985 cc filled up to a liter, will be normal.

12. The books generally recommend the proportion of normal solution of oxalic acid; this is inadvisable for many reasons. The above manner of using the pure acid BY WEIGHT IS by far the best and MOST ACCURATE. If a solution is wanted, only half normal should be made, since a normal oxalic acid solution is almost saturated.

Starting with oxalic acid, the normal alkali will be obtained first, and by its means the normal acid for use.

## 25. NEUTRALIZATION AND CALORATION.

1. THE NORMAL SOLUTIONS, prepared according to the methods indicated, are very useful. They permit the ready determination of the strength of given substances, as shown. They also enable us to establish chemical laws and determine important chemical equivalents.

2. Mixing equal volumes—measured by burette or pipette—of normal solution of base and acid, we obtain a NEUTRAL substance in solution; the process is called NEUTRALIZATION. If we take 10 cc N nitric acid and add 10 cc N potassium hydrate—careful evaporation will soon show the formation of the familiar prismatic CRYSTALS of potassium nitrate (15.10). In the same manner, sodium hydrate and muriatic acid yield the cubical crystals characteristic of sodium muriate or salt (11.8).

3. If the mixed solution is carefully distilled, a salt residue remains in the flask, and the distillate is pure water. Accordingly,  $KaH^{+}e$  and  $HNa^{+}e$  giving  $KaNa^{+}e$  and  $H^{+}e$  by double decomposition, (22, 2, 7), this HYDROGEN HYDRATE FORMED IS WATER. That is, equivalent amounts of acid and base neutralize each other, forming a salt and water. Thus we have a third kind of double decomposition, namely by neutralization.

4. If say 10 cc of normal solution are taken, the amount of the compound is exactly 10 milligramme-equivalents (24, 6). The mixture carefully evaporated to dryness or to crystallization, and completing the crystallization by spontaneous evaporation—the weight of the salt formed represents also 10 mgr. equivalents, and will allow the DETERMINATION OF THE EQUIVALENT OF THE BASE if that of the acid is known. The salt is the acid in which hydrogen has been replaced by the metal (18, 6).

5. Thus 10 cc normal solution of pure  $\text{Ka Hate}$  and as 10 cc normal solution of  $\text{H Sate}$  yield 10 milligramme-equivalents of crystals of potassium nitrate; the residue weighing 1010 mgr, the equivalent of  $\text{Ka Nate}$  is 101. But that of  $\text{H Nate}$  is 63, (18, 12); the difference  $101 - 63 = 38$  represents the excess of the equivalent of potassium over that of hydrogen displaced. Hence the EQUIVALENT OF POTASSIUM is 39. The corresponding residue of the sulphate is 870 mgr, that of the muriate 745 mgr; they give the same value for Ka.

6. Corresponding determinations with normal sodium hydrate solutions give the CHEMICAL EQUIVALENT OF SODIUM 23. In the same manner, the equivalent of AMMONIA is found to be 18.

For sodium, direct determinations of the equivalent are possible, though not as accurate, because the fresh cut sodium corrodes quite promptly, and the action of the water is rather too violent. See 18, 8, taking water instead of dilute acid.

7. Instead of measured amounts of normal hydrates, carefully weighed amounts of CARBONATES (16, 3) may be used exactly as the metal in 18, 8. If the carbonate is in form of crystal or cleavage piece (calcite), the solid may be placed on the slanting dry wall of the tube, as was the metal. If a powder, it may be weighed in a small porcelain boat, and this placed in the tube.

8. In this way, 12 cc gas (fixed air) are obtained from the following number of milligrams of NATIVE CARBONATES: magnesite 42, dolomite 46, calcite 50, siderite 58, smithsonite 63, strontianite 74, witherite 98, malachite 110, cerussite 133.5. Also from the following amounts of ARTIFICIAL CARBONATES: Na 53, Ka 70, Cd 86, Hgic 130 and bicarbonates: Na 42, Ka 50. All these weights are RELATIVELY EQUIVALENT, producing the same amount of fixed air.

9. It is easy to show that these numbers are true equivalents, or that EQUAL VOLUMES OF FIXED AIR AND HYDROGEN ARE EQUIVALENT. For if equivalent, the values for



Na and Ka carbonates give upon subtracting the equivalent of the metal (23 and 39) the same number 30 as the equivalent for  $\text{C}^{\text{ate}}$ . This subtracted from smithsonite, siderite, cerussite leaves for the metals Zn, Fe, Pb, the numbers 33, 28, 103.5, precisely as found before (18, 10 and 19, 12).

10. Accordingly, THE EQUIVALENT of  $\text{C}^{\text{ate}}$  is 30, and fixed air is equivalent with hydrogen, measure for measure. For dolomite 46, the metal equivalent is 16 which is half of that of the constituent metals Mg 12 and Ca 20. In the same way sodium bicarbonate gives 12 and potassium bicarbonate 20, exactly half the sum of the metal and hydrogen. From calcium we find 20, from calcite 50.

11. When equal volumes of normal acid and base are mixed, THE TEMPERATURE RISES ABOUT 7 DEGREES; a trifle more with sulphates, a little less with muriates. The unit of heat is the gramme-degree ( $\text{gr}^{\circ}$ ), the amount of heat required to raise the temperature of one gramme (cc) of water one degree (centigrade). Using 100 cc of each, 1400  $\text{gr}^{\circ}$  heat are produced by 100 milligramme-equivalents of acid and base.

12. One milligramme-equivalent of base uniting with one milligramme-equivalent of acid therefore produces a CALORATION OF ABOUT 14 GRAMME-DEGREES OF HEAT in forming a salt. Here only the soluble bases (alkalies) have been considered. Numerous accurate determinations of caloration have been made by THOMSEN of Copenhagen and BERTHELOT of Paris.

## 26. FLUX AND GLASS.

1. MANY SUBSTANCES ARE INSOLUBLE IN WATER AND IN ACIDS, even upon boiling. Quite a number of silicates and some precipitates are of this kind. Such are most of the gems (10) and the minerals Nos. 7 to 12 in 11, 5. Barium sulphate and silver muriate are the most common precipitates

insoluble in acids. To examine such materials in the wet way, they must be brought into solution.

2. To effect this, the insoluble material is most finely pulverized and mixed with a large excess of alkaline carbonates. The mixture is fused (FLUXED) in a platinum vessel, and maintained in the liquid state for some time. Ordinarily a DOUBLE DECOMPOSITION BY FUSION takes place, so that the cooled mass is partly soluble in water, and the residue left by water is soluble in acids.

3. For example, the absolutely insoluble Ba Sate precipitate, mixed with a large excess of Ka Cate gives, upon prolonged fusing, a mass from which water readily extracts the excess of Ka Cate taken and the Ka Sate formed by double decomposition. The residue of Ba Cate is insoluble in water, but readily soluble, with effervescence, in nitric acid, giving Ba Nate in aqueous solution.

4. The excess of Ka Cate in the first aqueous solution is removed by adding nitric acid until effervescence no longer takes place; then Ka Nate only is present in addition to the Sate, which in no way can interfere with the testing for that Sate.

5. In the same manner, Ag Mrate, fluxed with Ka Cate, yields Ka Mrate, which is extracted by water, together with the excess of Ka Cate taken. The residue of Ag Cate, insoluble in water, is readily dissolved by dilute nitric acid, giving Ag Nate. Thus also here, the acid is found in that portion of the flux soluble in water, the metal in that portion insoluble in water, but soluble in acids.

6. SILICATES, M Siates, fluxed in the same manner, give Ka Siate and M Cate. In this case, the entire fluxed mass is treated directly with dilute muriatic acid, causing the effervescence of fixed air and the separation of silicic acid in the GELATINOUS CONDITION. Evaporating to dryness, heating the dry residue gently till all acid vapors are driven off, the

metallic muriates will be taken up in water, while SILICA will remain, being insoluble.

7. In general, the compound insoluble in acids may be represented by  $M\text{Rate}$ , where M designates the metallic, R the non-metallic constituent. Fusing with excess of  $Ka\text{Cate}$  gives, by double decomposition,  $M\text{Cate}$  (insol.) and  $Ka\text{Rate}$  (sol. in water), together with the excess of  $Ka\text{Cate}$  not changed.

As a MIXTURE of Na and Ka carbonates is much more fusible than either carbonate taken singly, the mixture is preferred. Not less than four times the weight of the substance should be taken.

8. In some cases, it is advisable to add other fluxes to the carbonates or to take other fluxes instead; but the process remains essentially the same, namely, a double decomposition by fusion.

For simple TESTING, it suffices to fuse a little of the insoluble substance into a soda bead on the platinum loop.

9. The silica (6) dissolves readily in a soda bead on fusion, under lively effervescence of fixed air. This is a very simple test for silica. With enough silica, the bead remains transparent when cold; in fact, a GLASS has been formed. This glass being soluble in water, is called SOLUBLE GLASS. It is manufactured in quantity for various applications.

10. Ordinary GLASS, not soluble in water, nor in acids, is an AMORPHOUS DOUBLE SILICATE of Na and Ca (window glass) or Ka and Ca (crown glass). Flint glass contains also lead silicate. The carbonates mixed in proper proportions with silica, when fused and slowly cooled, give true, amorphous glass; when rapidly cooled, crystallization may take place, resulting in an opaque mass—not a real glass.

11. The quality of the glass produced depends on the proportion of the essential materials and their purity. Common

bottles have to be very cheap—hence they are made from lowest grade materials.

COLORED GLASS is obtained by small additions of metallic calxes, which dissolve, producing the same colors permanently as shown in the borax bead for a short time only. The Egyptians made good glass, mainly colored; the cut represents specimens thereof. Compare 5, 6.



12. SILICA, being absolutely non-volatile in our furnaces, drives out all other non-metallic constituents from salts, when heated therewith; for these non-metallic constituents are volatile, and thus cannot remain at such temperatures. Silica drives out all other constituents, not because it is stronger, or has greater affinity, but simply because it cannot get away, while the others, being volatile, can escape from the fiery furnace, and do so.

## 27. METALS AND RADICALS.

1. Having become familiar with the principal chemical processes and a considerable number of chemical substances, both native and artificial, it seems advisable to recapitulate a few of the general facts in order to find the best way forward in the study of chemistry.

2. First of all, we have learned to distinguish on INDIVIDUAL CHEMICAL SUBSTANCE from all sorts of mere mixtures. The crystal form, specific gravity, fusing and boiling point, and other properties, give as many criteria for the recognition of the individual chemical, and if need be, as many

methods of separation and purification expressed by the general term of FRACTIONING.

3. In this manner the metals, salts and acids have presented themselves as CLASSES or FAMILIES of chemical individuals. The metals, possessing that peculiar luster (metallic) and malleability. The salts, generally crystallizing from aqueous solution and by the blowpipe revealing the presence of a metal. The acids, dissolving metals under the evolution of hydrogen or other gases, with the production of salts.

4. The study of the solution of metals in dilute acids revealed the fact, that acids are hydrogen salts, or that the hydrogen in the acids corresponds to the metals in the salts. Solution of a metal in an acid is simply a substitution in absolutely FIXED PROPORTIONS BY WEIGHT, termed equivalents. These are referred to hydrogen as unit, or Mg as twelve (18, 10).

5. The salts and acids are evidently DUAL BODIES, consisting of TWO component parts. First, the metal in salts and the corresponding hydrogen in acids. This component we shall call the METALLIC CONSTITUENTS of salt and acid; for hydrogen is metallic in its character. The other constituent is NON-METALLIC, the salt and the acids responding to the same tests.

6. Thus, a drop of sulphuric acid, added to an acidified, dilute solution of barium nitrate, produces a white precipitate; so does the salt obtained by dissolving zinc or magnesium, or any other metal, in sulphuric acid. All these chemicals are therefore SULPHATES, namely H Sate, Zn Sate, -Mg Sate, etc. Now the question arises, what is this Sate?

7. We have abundant evidence that this Sate is volatile, and we can prove that it contains sulphur, both by SYNTHESIS and by ANALYSIS. Burning sulphur in a tube, carrying

the product of combustion through water, that water will soon give the reaction of sulphates with barium solutions, especially if a shaving moistened with concentrated nitric acid is placed in the course of the gas produced. Simply heating green vitriol in a glass tube, the odor of burning sulphur becomes manifest; that is, the green vitriol must contain sulphur.

8. But we also know that the non-metallic  $\text{S}^{\text{ate}}$  is not sulphur merely—for we have obtained copper sulphide by synthesis (21.8) and found it entirely different from blue vitriol, which is a sulphate.

Consequently the non-metallic constituent of sulphates consists of sulphur and something else; it is a complex material, called a RADICAL.  $\text{S}^{\text{ate}}$  is the radical of sulphates.

9. We have already determined the equivalent of this radical, and can now determine the equivalent of its constituents. The equivalent of sulphuric acid we found to be 49; but if  $\text{H S}^{\text{ate}}$  is 49, the radical  $\text{S}^{\text{ate}}$  has the equivalent 48. It contains sulphur; but  $\text{S}=16$ , leaves for the unknown part of the  $\text{S}^{\text{ate}}$  radical the equivalent 32.

10. In a like manner we have found the equivalent of the radical of CARBONATES to be  $\text{C}^{\text{ate}}$  30 (25.10). We know, by synthesis (16.9), that it contains carbon.

NITRATES of all kinds, being derived from nitre (13.9) or  $\text{K}^{\text{a}} \text{N}^{\text{ate}}$ , contain the radical  $\text{N}^{\text{ate}}$ , the equivalent of which is 62. The radical  $\text{M}^{\text{rate}}$  (MURIATE) has the equivalent 35.5, carried from common salts (18, 12). The exact nature of these radicals is also unknown.

11. But while the composition of these radicals of salts and acids is unknown, we can practically answer all questions about their ordinary reactions. If we wish to know how much salt is required to precipitate a given amount of silver nitrate, and how much silver muriate will be obtained, we have all the data required in the equivalents. Namely,  $\text{Ag}$  108,  $\text{N}^{\text{ate}}$  62,

Mrate 35.5, Na 23. Accordingly 170 Ag Nate requires 58.5 Na Mrate and will yield 143.5 Ag Mrate.

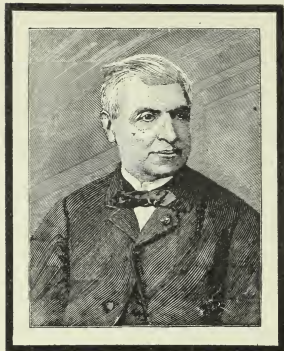
12. It is apparent that the sulphides (21) and iodides (23) are compounds of a different order. They consist of only two substances, the metal and the non-metal, S or Io. Such compounds are called BINARIES or binary compounds. They are named as exemplified. The terminal DE (from duo, two) with the essential part of the name of the non-metal (SULPH-ur) by the connecting vowel i.

## 28. CHEMICAL REACTIONS.

1. The principal chemical processes have been shown and employed in the preceding lessons. It will be advisable now to review and classify them. We shall find that but very few really different reactions exist. It must be born in mind, that chemists designate any chemical action by the word REACTION.

2. Ordinarily, a volatile substance and high temperature cannot co-exist; the volatile substance will escape. Hence, when water or other volatile liquids are present, no high temperature can be employed. Practically speaking, all chemical operations are therefore either in the DRY WAY or WET WAY, according as high temperatures or volatile liquids are used.

3. But if the volatile liquid be enclosed in a vessel strong enough to resist the rapidly increasing pressure of the vapor from within as well as the high temperature applied from without, the distinction between the two ways will become less marked. Since such vessels usually are constructed so as to close themselves more tightly, the greater the pressure of the vapor, they are termed AUTOCLAVES. The first autoclave was Papin's digestor.



G. A. DAUBRÉE.

Died May 28, 1896, at the age of 82 years.

4. Work with the autoclave is both difficult and dangerous. The old chemists had nothing corresponding to this, and modern chemists have restricted its use mainly to organic chemistry. In its simplest form, the autoclave is a strong glass tube, drawn out and closed by fusion, after the charge has been introduced. Daubrée and Friedel have used the autoclave in mineral chemistry. The first obtained fine crystals of quartz and pyroxene; the latter obtained feldspars and topaz crystals in that way.

5. Only THREE really different classes of CHEMICAL REACTIONS can be recognized, namely synthesis, substitution and double decomposition. In synthesis, two substances unite to form a new compound. In substitution, a substance takes the place of one of the two constituents of a compound. In double decomposition, two compounds mutually interchange their constituents, forming two new compounds.

6. A number of SYNTHESSES have been presented in the preceding lectures; especially the formation of sulphides (21) and iodides (23). The conditions under which two substances unite must be specially studied; the degree of temperature required is always an important factor.

The opposite of synthesis is ANALYSIS, the term taken in its broadest sense of separation. Such reactions will soon come before us.

7. SUBSTITUTION may involve the metallic or the non-metallic constituent of a compound. When a metal is dissolved in dilute acids (17) or when reduced in the wet way



(18), it is the metallic constituent which is replaced. When hydriodic acid is formed by hydrogen sulphide (23, 5) it is the non-metallic constituent that is replaced.

8. Of DOUBLE DECOMPOSITIONS we must distinguish four kinds, namely by neutralization (25, 3), by volatilization (22, 2), by precipitation (22, 7), and by fusion (26, 2). Of these four, the first is erroneously considered a synthesis of acid and base; for water ( $H\ H^{ate}$ ) actually forms, as well as the new salt. The last depends largely upon an excess of the flux.

9. In the case of precipitation, it is clear that insoluble compounds cannot stay in solution; hence two compounds, containing separately the ingredients of an insoluble compound, will produce a precipitate when brought together in the same liquid. This rule was first given by Berthollet (p. 32). Accordingly, if an insoluble compound is to be prepared, mix two solutions, the one containing the metal, the other the radical of that compound.

10. If two substances, containing the constituents of a volatile compound are exposed to a temperature higher than that at which the volatile compound boils, it cannot remain and will pass over as gas or vapor. This is the second rule of Berthollet.— $H\ N^{ate}$  drives out  $S^{ide}$  at common temperature from  $Ka\ S^{ide}$ . The  $Ka\ N^{ate}$  remaining, heated on a sandbath with  $H\ S^{ate}$ , gives a distillate of  $H\ N^{ate}$ . The  $Ka\ S^{ate}$  remaining, heated to redness with silica, gives a residue of  $Ka\ S^{iate}$ . The  $S^{ate}$  decomposes as it is driven off.

11. It is therefore of the highest importance to know the VOLATILITY and SOLUBILITY of compounds, in order to understand chemical tests and the methods of preparation of chemicals. The rules of Berthollet then will be the most valuable guides. For example, let  $Ba\ S^{ate}$  be wanted. Being quite insoluble, it will form as precipitate if to ANY  $Ba$  Solution we add the solution of ANY sulphate. Therefore, take the common  $Ba\ M^{ate}$  and add  $H\ S^{ate}$ , and  $Ba\ S^{ate}$  will precipitate.

12. These RULES OF BERTHOLLET (p. 32) even apply to cases merely difficultly soluble. For example, by the Gay-Lussac lines of solubility (p. 70), it appears that the solubility of nitre rapidly increases with temperature, much more so than that of Chili saltpeter, while salt ( $\text{Na Mrate}$ ) hardly increases in solubility. Accordingly, the high priced  $\text{Ka Nate}$  is made (by conversion) by dissolving the cheap Stassfurth  $\text{Ka Mrate}$  ( $\text{Ka Clide}$  on Chart) in boiling water, and adding cheap Chili saltpeter; common salt will separate, and from the hot solution nitre will crystallize on cooling.

---

NOTE.—DIAGRAMS OF REACTIONS should be written out in the simplest possible manner. The essential features of the reactions should be specially marked, namely insolubility, volatility, etc. The substances actually taken are written one above the other; the DETERMINING REACTION is now marked by one heavy line terminating in an arrow, and the CONSEQUENT REACTION is marked by a light double line. For gases and vapors, the line should be drawn upwards; for precipitates the line should be drawn downwards, as shown in the few instances here given. The diagram represents four characteristic cases, and needs no further explanation. The student should acquire the habit of writing out every reaction in this manner.

COMPLEX REACTIONS are simply two or more of the simple reactions described, succeeding one another at shorter or longer intervals of time. As an example, the gradual change of  $\text{Ka Side}$  to  $\text{Ka Sate}$  is shown in the diagram.

## 29. COMBUSTION AND PHLOGISTON.

1. The heat of the sun gives motion to all things on this globe. Without the central luminary, no life could exist on the earth. When man succeeded to make a fire for his own use, he took the greatest step towards civilization. The Greek myth of Prometheus voices the recollection of the race.

2. In science, both physical and chemical, heat and light occupy an equally prominent place. In chemistry, heat is one of our principal powers for effecting changes of matter. The operations in the dry way range from blowpipe tests to the

smelting of iron and glass in gigantic furnaces. Modern progress largely is brought about by the use of our mineral combustible, coal giving both heat and power.

3. The phenomenon of combustion itself is one of the greatest questions in chemical science. As the sun seems to rise in the east of the observer, himself at rest in the restful landscape, so the combustible when burning seems to set free heat in flame (phlox or phlogion) and glow, leaving behind but a little of ashes or calx. The main part of the combustible seems to be PHLOGISTON.

4. But long continued and most careful observation of the stars finally convinced COPERNICUS that it is the sun which is at rest, and not the earth. In a like manner, LAVOISIER has demonstrated, that the combustible does not diminish, but greatly increase in weight during the process of combustion. Lavoisier is the Copernicus of chemistry.

5. These general reflexions form a necessary introduction to the chemical study of combustion, which we now will enter upon. It will soon become apparent that this term cannot be restricted to flame and fire, but applies equally to phenomena of world wide extent, but so slow and so wide diffused, that neither flame nor visible glow attend them.

6. It was the German chemist GEORG ERNST STAHL (1660-1734) who first (1697 and especially 1717) grouped all phenomena of combustion and tried to explain them by the hypothesis of phlogiston. All combustible materials were supposed to contain phlogiston; wood, oil, fat, wool, also grain and of mineral materials, metals, coal and especially sulphur.

7. According to this theory, the metals are compounds of the metallic calx and phlogiston. Heating metallic lead before the blowpipe, it burns, that is, phlogiston is set free; the calx remaining as incrustation on the charcoal, is simply the other constituent of the metal.

8. Now metals are more or less readily calcinated, that is, more or less combustible, as has been exemplified in the

seventh lecture. Charcoal is much more combustible than any of the common (heavy) metals. This is evident because we can burn all kinds of coal in an iron stove without consuming the iron.

9. In the phlogiston theory of Stahl, the metal must contain less phlogiston than coal. Consequently, when metallic calxes, intimately mixed with carbon, are heated, the carbon transfers its phlogiston to the metallic calx. The metal (calx and phlogiston) is reproduced.

10. But this phlogiston which is supposed to readily leave carbon and unite with the calx to form the metal, was never produced in the free state; and when weighed amounts of metals, like tin, were calcined, they notably increased in weight, as already shown by Jean Rey, a pharmacist of Bergerac, in 1629.

11. When hydrogen gas had been discovered by Cavendish, it was supposed to be phlogiston, or the fire-matter of Stahl. Cavendish himself remained a defender of the phlogiston theory till his death (1810).

12. For nearly a century this phlogiston theory reigned supreme. The apparently conflicting facts were not recognized. Within a very wide circle of facts, the theory seemed to explain everything satisfactorily. Like the Ptolemaic system of the world, it was considered to be in strict accordance with the everyday testimony of the senses. To doubt it was almost a crime, especially in Germany.

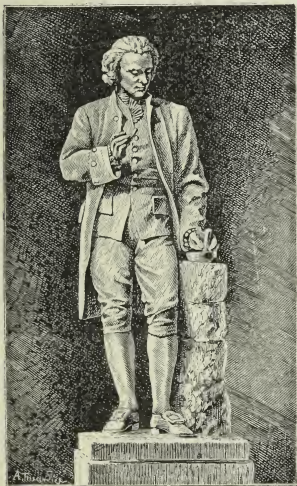
### 30. COMBUSTION AND OXYGEN.

1. It would be very interesting to study the history of the CHEMICAL REVOLUTION (Berthelot) which marked the last quarter of the eighteenth century, but time forbids. It will be necessary to confine ourselves to the most conclusive experiments, independent of their historic order.

2. A weighed piece of magnesium wire, burnt over a weighed dish, will show quite a large INCREASE IN WEIGHT, though the violence of the combustion makes a partial loss of the calx unavoidable. Under most favorable circumstances, this increase in weight is about two-thirds of the weight of the metal taken.

3. IN THE WET WAY the calx of a metal may be obtained by dissolving the metal in nitric acid, evaporating and igniting; the residue is the calx. Such determinations have been made by Berzelius (p. 22). Lead increased almost 8 per cent., mercury fully as much, and copper 25 per cent. There can be no doubt about the increase in weight in calcination.

4. Lead converted into nitrate gains 60 per cent. (19, 12).



PRIESTLEY STATUE.

Igniting the nitrate in a tube, rutilant vapors first appear in abundance, then a colorless gas; a shaving with but a single glowing point, will burst into flame when held in this gas. Priestley made this experiment 1772; the gas he called "de-phlogisticated air." Its main character is that it SUPPORTS COMBUSTION.

5. Mercury heated for a long time steadily to near its boiling point is slowly converted, especially on the surface, into a RED crystalline powder, called "precipitate per se" also simply RED PRECIPITATE. It is the calx of mercury. In the wet way it is prepared much more rapidly, in the manner above stated (3).

6. Heating this red precipitate in a tube, it first turns dark brown, then drops of metallic mercury appear on the cold parts of the tube. At the same time a colorless gas is evolved, the amount of which may be measured by our gas burette. Tested as above stated, it supports combustion, or is dephlogisticated air. Lavoisier, who made the same experiments soon after, finally called this gas OXYGEN. Scheele had called it fire air.

7. OXYGEN GAS, collected in the usual way, is shown to be colorless, odorless, energetically supporting combustion; it is slightly heavier than atmospheric air.

It was first liquefied in 1877, by Cailletet and Pictet; its critical point is at 118 degs. below zero; 50 atmospheres pressure liquefies it at that temperature.

8. Oxygen is most readily OBTAINED IN QUANTITY by moderately heating the salt known as potassium chlorate, which crystallizes in thin (oblique) rhombic tablets of 104.4 degs. This salt first fuses, then decomposes, often with explosive violence. When it is mixed with pulverized pyrolusite (9, 7), the decomposition begins at a lower temperature and is entirely safe and without violence.

9. COMBUSTIONS in oxygen gas are most beautiful and instructive, if performed in combustion tubing of hard glass, connected through the drying columns with the generator, and on the other end with suitable absorption flasks for the products of combustion. Some of the substances to be burnt are better placed in porcelain boats. This method of experimentation is under perfect control of the operator, and much more instructive to the student, than the common way with large flasks.

10. CARBON (small prisms of blowpipe charcoal) burns with a brilliant white light; the product is fixed air (16). SULPHUR burns with a blue flame; the product is a gas, bleaching blue litmus after having turned it red. PHOSPHORUS burns with flame, emitting a most dazzling white

light and giving a solid, white product of combustion, which dissolves in water, to an acid (phosphoric). **MAGNESIUM** and **ZINC** burn also with brilliancy—the first giving white, the second green light. **SODIUM** burns with dazzling yellow light.

11. Several of these combustions can be shown to still greater advantage by using the **COMPOUND BLOWPIPE** (5, 9), connecting the inner tube with the oxygen supply. **STEEL** watch springs burn in this flame, producing a magnificent shower of brilliant sparks of burning steel. **PLATINUM** wire melts readily in this oxy-gas flame. **LIME** emits a most dazzling white light when held in this flame; this is the so-called calcium light.

12. **PRIESTLEY** discovered “dephlogisticated air” 1774



SCHEELÉ.

in England. **SCHEELÉ** produced, entirely independently, at about the same time, his “fire-air” in Sweden. Both remained firm believers in the phlogiston theory, although they had produced the “eminently respirable gas” of **LAVOISIER**, which he afterwards called oxygen. Too often, modern science forgets this lesson; thought is as important as fact. The old “ora et labora”

scientists should read, “think and work.”

NOTES 8. Oxygen gas need not be collected in bag or gasometer beforehand; it may be generated while the experiments in combustion (9) are exhibited to the class.

In the **DRY WAY**, it is most elegantly generated by filling the mixture of chlorate and pyrolusite (black oxide of manganese) in a combustion

tube and heating this in the combustion furnace. By properly regulating the gas flames as to size and number, the flow of oxygen can easily be kept exactly as wanted. The gas should be dried in columns, and passed through a little concentrated sulphuric acid in a wash bottle (with straight safety tube) before it reaches the tube in which the combustion is effected. The mixture should be dry, fill the entire length of the combustion tube, but only about two thirds of its width. The heating should begin nearest the drying columns. The total amount of oxygen for all combustions is very small, when they are made as stated in the text, in combustion tubing of about one inch diameter. The wash bottle with concentrated sulphuric acid is mainly inserted to show the rate at which the gas flows.

In the WET WAY, oxygen is generated during my lectures exactly as hydrogen. The Kipp is charged with lumps of pyrolusite and commercial (10 volume) peroxide of hydrogen to which, cautiously and in small doses, about one twelfth volume of concentrated sulphuric acid has been added. This process is perfect; of course, the gas is rather expensive when obtained in this way. It is readily understood that the volume is about twenty times that of the liquid reagent used.

The generating liquid must be drawn off at the close of the hour or day; it deteriorates in keeping.

9. The combustion of the SODIUM is most brilliant and most conveniently performed in an iron deflagrating spoon; light the metal (thoroughly freed from the naphtha) by the flame of a Bunsen burner, then direct a jet of oxygen gas upon it by means of a glass tube. For obvious reasons it is advisable that the experimentator wear a mask or watch the combustion through a pane of blue glass larger than the face.

The form of experimentation described in the books is much less brilliant in results, comparatively clumsy and wasteful, and finally much less instructive.

The sodium oxide produced contains enough peroxide to give the peroxide of hydrogen reactions when dissolved in water.

11. When time and means allow, the OXY-HYDROGEN BLOWPIPE should be used, and the most striking experiments indicated above, should be repeated. In this case, the substances may be most conveniently supported on charcoal or cupels, which again may stand on a Battersea scorifier supported on the ring stand.

29, 4. That Lavoisier is the Copernicus of Chemistry was first brought out in the French *Resumé* of my *Atomechanik*, 1867.



## 31. OXIDE AND RADICAL.

1. The compounds which form when metals burn are now understood to be OXIDES, consisting of the metal and oxygen. All metallic calxes, made by heating the metal in air, must be oxides; in other words, oxygen must be a constituent part of atmospheric air. This was demonstrated by LAVOISIER, as shall be shown in the next lecture (see Frontispiece).

2. The metallic calxes prepared in the wet way, being identical with those obtained in the dry way, therefore also are oxides. Accordingly, the determinations made by Berzelius (30, 3) are really determinations of the equivalent of oxygen. If mercury (equiv. 100) increases 8 per cent. the equivalent of the oxygen is 8. Copper, having an equivalent of almost 32, increases 25 per cent., that is 8, which is the equivalent of the substance combined with copper, or the oxygen.

3. SYNTHESIS OF WATER. Water, forming in the combustion of hydrogen gas (17, 8), therefore is hydrogen oxide. The exact proportions by weight of oxygen and hydrogen in water were first determined in 1841 by DUMAS (p. 25). The hydrogen was carefully purified and dried (17, 5), passed over copper oxide in a combustion TUBE resting on tiles barely glowing red; water forms, condensing in the GLOBE to a liquid; to avoid the escape of traces as vapor, the globe is followed by a light absorption tube. The black copper oxide is gradually turning red, being reduced to metallic copper.

4. This is not the place for a discussion of the details of this determination of one of the fundamental data of chemical science. Such a discussion the author has published, 1894, in his *True Atomic Weights*, pp. 176-183. The errors involved in more recent determinations by chemists using more elaborate and complex processes have also been indicated (pp. 185-189).

5. The weight of the combustion tube with copper oxide, diminished by the weight of the same tubes at the close of the operation, when the black oxide has been reduced to metallic copper, evidently gives the weight of the oxygen consumed to form the water. The weight of the water formed is the increase in weight of the globe and absorption tube. In all experiments the proportion of the weight of the oxygen to that of the water is found as 8 to 9 exactly. Hence the hydrogen used weighed one. Consequently, the equivalent of oxygen is 8, exactly.

6. A CHEMICAL FORMULA (IN EQUIVALENTS) REPRESENTS ONE EQUIVALENT OF THE COMPOUND BY THE SYMBOLS OF THE EQUIVALENTS OF THE COMPONENTS. The symbols, when representing an equivalent, we shall print in *italics*.

Thus, the chemical formula of water is *HO*. This formula expresses the simple FACT that one equivalent of hydrogen,  $H=1$ , and one equivalent of oxygen,  $O=8$ , are contained in one equivalent of water  $HO=9$ .

7. DUMAS (p. 25) also established the true equivalent of carbon, by burning a weighed amount of diamond in a current of pure oxygen gas, and weighing the amount of fixed air produced, collected in strong potassium hydrate solution contained in proper absorption tubes. The details are found in the author's True Atomic Weights, pp. 19-24, p. 147, and pp. 176-177. The weight of the carbon burnt is to the oxygen taken up as 3 to 8 exactly.

8. Accordingly, the equivalent of carbon in fixed air would be 3, and the chemical formula of fixed air would be *CO*. But Chemists have assumed for reasons that need not be stated here, that there are two equivalents of oxygen ( $=16$ ) in fixed air to one of carbon. The experimental proportion of 8 to 3 then compels the adoption of 6 as the equivalent of carbon and the formula of fixed air becomes *CO<sub>2</sub>*. For that reason fixed air is commonly called CARBON DIOXIDE.

9. We can now establish the composition of THE RADICALS in carbonates and sulphates. The radical Sate (27, 9) has the equivalent 48. Direct experiments have shown that it contains but one equivalent of sulphur, 16; hence the oxygen weighs 32, representing four equivalents. Consequently the equivalent formula of the radical Sate is  $O_4S$ . Sulphuric acid has the formula  $H\ O_4S$ . The following formula represents an equivalent each:  $Na\ O_4S$ . —  $Cu\ O_4S$ . —  $Pb\ O_4S$ . —  $Ag\ O_4S$ .

10. Direct experiments of this kind were made by v. HAUER, 1857. Heating a weighed amount of cadmium sulphate in a current of dry hydrogen sulphide gas, he obtained a residue of sulphide weighing 69.23 per cent. of the sulphate taken. Nine careful determinations were made. Now, since the equivalent of Cd is 56, that of S 16, Cd Side is 72, and  $Cd\ O_4S$  should be 104. But 72 is exactly 69.23 per cent. of 104. The formula of Sate is therefore correct.

11. The radical of carbonates was found to have the equivalent 30 (27, 10). It contains only one carbon, therefore three of oxygen, or Cate is  $O_3C$ .

For magnesium carbonate  $Mg\ O_3C$  this gives 42. Ignition leaves the oxide,  $Mg\ O=20$  or 47.62 per cent. Actual determinations made by SCHEERER in 1850 on Magnesite from Frankenstein gave 47.63 per cent., thus confirming the above.

12. For carbonates and sulphates the radicals are now known. The third constituent has been found to be oxygen. Its equivalent is 8, that of hydrogen being one. In carbonates enter three equivalents of oxygen with the equivalent of the metal and the carbon. In sulphates there are four equivalents of oxygen.

The radicals of nitrates and muriates we must leave undetermined for a short time.

## 32. ANALYSIS OF THE AIR.

1. The terraqueous globe is completely surrounded by the air as by a mantle, protecting us equally against the cold of cosmical space and the burning heat of the sun. In this air-mantle float the clouds, the vapors sent up from the earth and sea by the sunbeam; they descend again as rain and snow. Into this air-mantle passes dust and smoke from factory and fire. Therefore, we call it with the Greeks, the ATMOSPHERE.

2. AQUEOUS VAPOR is present in the air in greatly varying proportions. We are sensitive to both an excessive amount and to a deficiency thereof. Air at any given temperature can contain a definite amount of vapor only; it then is saturated, and a good HAIR HYDROMETER indicates 100 per cent. moisture. During certain southwest winds in summer, the humidity of the air may run down to less than 10 per cent; moving air of this character (dry winds) scorches vegetation.

3. In these United States, about two hundred million tons of coal—worth two hundred million dollars—are taken from the mines and burnt every year (12.10), returning something like 530 million tons of fixed air to our atmosphere, together with smoke and ashes. Animal life, in the act of respiration, also sends enormous quantities of fixed air into the atmosphere. Plants, we shall learn, take up this gas, decompose it by the aid of the sunbeam, and thus maintain a sort of equilibrium.

4. The chemical examination of atmospheric air must, therefore, begin with the determination of the amounts of moisture (water) and fixed air (carbon dioxide) present in the same. Effective absorbents (17, 5, 6), contained in light glass vessels of suitable form for accurate weighing, will retain these separately. The increase in weight of these vessels will tell the amount of water and carbon dioxide in the volume of air that has passed through them.

5. The simplest means of drawing air through a series of vessels is by means of the ASPIRATOR. Any flask or jug may be used as such, if closed with a doubly perforated stopper, provided with siphon, reaching to near the bottom of the flask and lengthened by rubber tube outside, while the other perforation by means of a short tube connects with the set of absorption vessels. The volume of the water flown out is equal to the volume of air drawn through. Special aspirator flasks, with a lower side-tubulature, are in the market.

6. As a rule, the moisture is absorbed by fragments of pumice, soaked with concentrated sulphuric acid, and kept in so-called U-TUBES, now elegantly made with ground glass stoppers and with short glass tubes for making connection. The carbon dioxide is absorbed by a strong solution of caustic potassa, contained in some of the varied forms of POTASSA BULBS, first introduced by Liebig (p. 23). Further details belong to practical chemistry.

7. Such determinations have shown that the amount of water varies enormously, as was anticipated; they have also shown the entirely unexpected fact, that the amount of carbon dioxide varies but very little in the atmosphere. In round numbers it amounts to three volumes in ten thousand volumes of air.

8. Pure and dry atmospheric air can be obtained by drawing common air through a set of absorption tubes of suitable size, to the vessel where the air is to be used. See 17, 6. If necessary to exclude all moisture and carbon dioxide, a TEST SET of U and bulb tubes, inserted between the absorption columns and the receiver, must show no increase in weight.

9. If now a measured volume, say 100 cc, of such pure air be slowly passed over pure copper gauze, heated to a low redness in a combustion tube, connected with a strong glass receiver, which as well as the tube with copper, was completely evacuated by a mercurial air pump, the copper will turn black, combining with the oxygen of the air. The resi-

dual air measures 79 cc, so that 21 cc were oxygen. Dumas (p. 25) and Boussingault.

10. This residual air is colorless and odorless; it does not support combustion nor life. For the latter reason, Lavoisier called it AZOTE and many French chemists continue to use the symbol Az for this gas. We call it NITROGEN, and represent by the symbol N. Careful weighings have shown it to be lighter than oxygen, in the proportion 7 to 8. Nitrogen has been liquefied. Its critical temperature is  $-146$  degrees, its critical pressure 35 atmospheres.

11. The first decisive demonstration of the composition of atmospheric air was made by Lavoisier. Our frontispiece pictorially commemorates this great event. Mercury was kept near its boiling point for twelve days and nights continuously; then the red precipitate first formed no longer showed increase, nor the volume of air any decrease.

After cooling, the residual air measured 42 to 43 cubic inches; originally 50 cubic inches had been taken. This shows a reduction of about 15 per cent in the volume of air. The residual air proved to be azote.

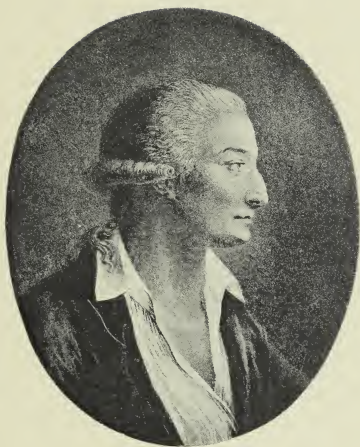
12. The red precipitate formed weighed 45 grains. Heated, it left 41.5 grains of metallic mercury, yielding 7 to 8 cubic inches of gas, proving to be oxygen.

When, in other experiments, the amount of oxygen so extracted by mercury and set free again from the red precipitate, was mixed with the inert residual air (nitrogen), the gas MIXTURE resulting was in every way identical with atmospheric air.

This completed the analysis and synthesis of atmospheric air.

---

NOTE. The discovery of DEPHLOGISTICATED AIR BY PRIESTLEY gave chemists a new gas of wonderful properties, only to involve chemical processes into greater confusion and deeper mystery. The FIRE AIR, discovered independently by SCHEELE, brought some light into the chemistry of the air, but most of the processes employed by him were so indefinite as to make it difficult even to-day to express them in formulæ.



**LAVOISIER.**

1794.





It is, therefore, natural, that both PRIESTLEY and SCHEELE remained faithful to the phlogiston theory, according to which metals lose something (phlogiston) when calcinated (dephlogisticated).

LAVOISIER, the Copernicus of chemistry, pierced the veil of phenomena that had hidden the truth to all previous investigators. He had only the same facts and materials which were also in the hands of the English and Swedish chemists, who both were most eminent investigators of the empiric or purely experimental school.

Lavoisier as an experimenter was not superior to Priestley or Scheele. It is true he possessed unlimited means to obtain all appliances he might desire; but his brilliant discoveries, so far as apparatus was concerned, might have been made equally as well by the poor apothecary of Koeping. Surely, there never was a chemist who was so entirely independent of pecuniary means as Scheele, whose very mind seemed to create all the appliances he needed. Priestley also was very successful in doing much with little. His own claims of having made his discoveries accidentally, is one of the oddities of his character; for his writings bear witness that he planned his experiments carefully.

Lavoisier was not a specialist; he was not merely an experimenter, for he was also a profound thinker. His studies ranged from mathematics to geology and physiology. He had mastered the fundamental and essential parts of the science of his day, as did the great philosophers of old. To this he added the especial research in the more limited field of the chemical processes. His mind directed the work of his fingers; and when in this manner, any fold of the veil of appearances was displaced, his mind was able to read the new form in accordance with the eternal ideal.

In this way the material gathered by the skillful workmen anywhere, in England or in Sweden, were refined and perfected in his hand and placed by his mind in harmony with the universal laws of nature, sufficiently so to find the eye point of the grand perspective; and so a revolution in chemistry was accomplished, exactly corresponding to that effected by Copernicus in astronomy two and a half centuries earlier.

The sun and the stars move around the earth, resting in the center of the world; so the senses declared before Copernicus, so they do to us. But Copernicus mentally placing his eye in the sun, saw clearly the true system of the world, and we now understand the mocking of our senses.

In a fire, the wood is consumed, the flame seems but a part of the wood, and the ashes are all the rest, so testifies our bodily eye. The same general relation Stahl declared to be true for the metals; they consist of the calx AND phlogiston. But the mental eye of Lavoisier saw the calx result from a union of the metal with a spirit invisible to the bodily eye, but sensible to the pointer of the balance. He isolated a portion of the matter, made it complete an entire metamorphosis by synthesis and analysis—and the vision appearing to his mind had become the starting point for the work of a century.

### 33. NITROGEN, PHOSPHORUS <sup>AND</sup> ARGON.

1. The alchemists, in their search for the elixir, subjected all kinds of animal materials to their operations. Brand, at Hamburg, in 1669, while doing such work, produced the true phosphorus. This discovery created the greatest sensation at the time. Having concentrated urine by freezing or by evaporation, he distilled the residue, mixed with sand and charcoal dust, gradually increasing the temperature. Now phosphorus is extracted from bones.

2. PHOSPHORUS is a soft, colorless (or faintly yellow) solid, of a specific odor. G 1.83, F 44 degrees, B 278. It is exceedingly combustible and readily inflammable; it must be handled with great care and is kept under water. Exposed to the air, it shows a glow of light in the dark, whence its name (light-bearer). It burns with extreme brilliancy in oxygen, giving solid, white phosphoric oxide, which dissolves in water to phosphoric acid (30, 10).

3. The great combustibility of phosphorus permits an approximate analysis of atmospheric air to be made as lecture experiment. In a pneumatic trough is placed a tripod supporting a scorifier on which is placed a coupel with a well dried piece of phosphorus. An open, well dried, bell glass is set over the tripod, and resting on three pieces of lead. The water should be at least three inches below the scorifier.

4. The phosphorus is ignited by touching it with the heated end of a wire, when promptly the bell glass is stoppered. The burning phosphorus fills the glass with a cloud of white oxide so dense, that no outline of the objects inside can be distinguished. The surface of the water is first depressed (due to expansion) but soon begins to rise, marking the consumption of the oxygen.

5. The combustion ceases. The white cloud gradually disappears, the oxide being dissolved in the water to phosphoric

acid—indicated by the blue litmus, that had been added to the water, changing to red. When no further change in the level of the water takes place, the water inside will be seen to occupy about one-fifth of the volume originally occupied by air.

6. To examine the character of the residual air, fill the trough sufficiently so that the level outside again stands even with the level inside the bell glass. Then remove the stopper to introduce the various tests, such as a burning wax taper, which will be extinguished. The apparatus being promptly stoppered after each test, can be left on the table till the next day. Then filling with oxygen equal to the original volume, and after equallizing level of water, the air will soon show the properties of atmospheric air. All the essential features of the subject will be recognized in this form of experiment, which is perfectly safe.

7. In the wet way, pyrogallic acid quite promptly absorbs oxygen from the air, if an excess of caustic alkali be present; the reagent turns deep brown. This method, due to Liebig (p. 23), is very quick and sufficiently exact. It can be used over mercury or with a gas burette, connected with an absorption gas pipette.

8. A shower of electric sparks, passed through atmospheric air, near the surface of water (or better, a solution of caustic potassa) soon reduces the volume considerably. If the water was tinted with cochineal, it will show acid reaction. From the alkaline solution nitre can be obtained. Nitric acid has evidently been produced. This accounts for the presence of nitric acid in rain water during thunderstorms.

9. Cavendish, who first made this synthesis of nitric acid from atmospheric air and water, added pure oxygen whenever the volume diminished no longer. But he found it impossible to convert the entire volume of air into acid; about one per cent. of the original volume remained.

10. These remarkable results of Cavendish were overlooked an entire century, till Lord RALEIGH, by another

method, obtained the same non-absorbable residual volume of nitrogen. He calls this gas ARGON. The density of argon exceeds that of nitrogen 50 per cent.

11. When absolutely dry nitrogen gas, entirely free from oxygen, is passed over magnesium heated to barely beginning redness in the tube of a combustion furnace, the nitrogen combines with the metal. The magnesium nitride formed is a brownish solid.

This property of magnesium has recently become very useful for the extraction of argon from atmospheric air.

12. When magnesium nitride is moistened, the odor of ammonia is produced.  $\text{Mg N}^{\text{ide}}$  and  $\text{H}^{\text{ate}}$  give  $\text{H N}^{\text{ide}}$  (ammonia) and insoluble  $\text{Mg}^{\text{ate}}$ . A mixture of hydrogen and nitrogen gas, in the presence of an acid, exposed to a shower of electric sparks, gives the ammonium salt of that acid. This reaction corresponds exactly to that of Cavendish (9).

## 34. BATTERY AND DYNAMO.

1. The chemist of the present has two physical powers at his service, namely HEAT AND ELECTRICITY. The chemist of antiquity only possessed the first, and that in but the narrow limits from the freezing of water to a white heat. To-day, the chemist employs temperatures from the freezing point of oxygen to the boiling point of carbon, and uses electricity at his pleasure.

2. The application of electricity in the chemical arts dates from the beginning of this century, when VOLTA (p. 31) constructed the galvanic BATTERY, the Voltaic pile. In the great chemical industries, electricity could not be used until the DYNAMO had cheapened and enlarged its flow by drawing it from a common coal fire and from cataracts.

3. The voltaic pile consisted of pairs of plates of copper and zinc, separated by a moistened rag (1800). Soon the plates were enlarged and each pair placed in a distinct vessel, containing water; such single CELLS united constitute the BATTERY. Water being replaced by salt solution or by dilute acid, increased the power greatly, but shortened its duration. Most of the zinc was wasted, being consumed without producing electricity.

4. Zinc in dilute acid dissolves with evolution of hydrogen. Pour a little mercury into the vessel, and the evolution stops, the zinc having become amalgamated, or coated with mercury on its surface, and mercury is insoluble in dilute acid. Pour some of the acid on platinum foil in another tube—no solution will take place, no effervescence will be seen, for platinum requires even aqua regia for its solution.

5. But pour the balance of the first glass on this platinum, so that the amalgamated zinc rests upon, or at least touches the platinum foil; instantly the evolution of hydrogen will begin again and be more abundant than with the zinc alone. Furthermore, the hydrogen does no longer seem to rise from the zinc, but from the insoluble platinum. This continues till the zinc or the acid is consumed.

6. Both the amalgamated zinc and the platinum, taken separately, are insoluble in the dilute acid. Even simply lifting the platinum up in the acid, so that the platinum no longer touches the amalgamated zinc, stops the evolution of gas completely. The amalgamated zinc IN CONTACT with the platinum is soluble in dilute acid, when not in such contact it is insoluble.

7. Such an action is called galvanic; it involves the production of an electrical contrast between the two metals, the amalgamated zinc and the platinum. Accordingly, in a galvanic cell, if the zinc is not to be wasted, but only to be used for the production of the current, the zinc must be thoroughly

amalgamated. In that case it can dissolve only while the contact is produced by closing the circuit.

8. But even such a cell is not constant yet. The other plate—copper—is seen to become coated. Daniell prevented this by placing the copper in a solution of blue vitriol, when pure copper deposited while the current is used. The simplest construction of this kind we have in the GRAVITY CELLS—copper plate in heavy blue vitriol solution below, the zinc plate in lighter dilute acid above.

9. The most effective cells yet constructed, are those of Grove and Bunsen in which copper is replaced by platinum (Grove) or carbon (Bunsen, p. 24), and kept pure by being inserted in concentrated nitric acid. As this acid would rapidly dissolve the amalgamated zinc, the nitric acid with the Pt or C is contained in a POROUS CUP, which again is set in the dilute acid contained in the glazed cup holding the zinc.

10. When such a cell is closed—that is, the carbon united with the zinc by a copper wire (conductor), the chemical action sets in, and an electric, or rather galvanic current flows through the wire—the circuit. Zinc dissolves as zinc sulphate in the outer cup, THE HYDROGEN PASSES THROUGH THE DILUTE ACID AND THE POROUS CUP, to be oxidized to water when it reaches the concentrated nitric acid. This is also evidenced by the rutilant vapors and red to green coloration of the acid. The acid gradually becomes dilute, but the carbon remains free from gas. THE CELL IS CONSTANT.

11. That a galvanic CURRENT passes through a closed circuit is readily shown by the production of heat and magnetism in the circuit. The first, by inserting a thin iron or platinum wire, gradually shortening it, till it glows red hot, white hot and finally melts. The second, by winding the circuit wire around soft iron, which becomes a temporary magnet while the circuit is closed—an electro-magnet.

12. With such electro-magnets, powerful machines are constructed, the so-called electric MOTORS, seen on our street

railways and in our shops. The best of these are REVERSIBLE, that is, if moved by any mechanical power (steam, hydraulic turbine) the motor produces electricity; it is then called a DYNAMO. These furnish the electricity required in modern chemical works.

---

NOTES. Four Bunsen cells joined in series, answer for all necessary experiments. The hydrogen current going in each cell from the zinc through the liquid to the other solid (C, Pt, Cu in the different kind of cells) the galvanic current is considered to flow in the same direction, so that the exposed carbon (or Pt, Cu) is considered the POSITIVE POLE of each cell, and the ZINC THE NEGATIVE POLE. Copper wires (best insulated) attached, carry the electrical power of these poles as good conductors; when these two wires are brought into metallic contact, direct or through any special apparatus, the CIRCUIT is said to be CLOSED, the current will pass and do its work.

Attach a file to one of these wires, and draw the other wire along the file; a shower of sparks of burning steel will be seen, especially brilliant if a thick wire coil be inserted. The production of heat, magnetism and motion has been referred to in the text proper.

For some purposes, the current is intensified by INDUCTION. A PRIMARY COIL of heavy wire is introduced in the circuit, which is automatically broken and closed in rapid succession by an iron armature attached to a spring. A very long and very thin copper wire, thoroughly insulated, forms an outer SECONDARY COIL around the first coil. Connecting the terminals of this secondary coil with tubes containing various gases under low pressure, they will be illuminated by the discharge (Geisler's and Plucker's Tubes). Even a shower of sparks will pass through air between balls or wires brought into proper distance, when connected with the terminals. Electricity thus produced in a near conductor, not in metallic contact with the primary conductor, is considered produced by induction. Coils of this kind are called INDUCTION COILS. The forms devised by Ruhmkorff are the best.

The great subject of electric induction was mainly established by the researches of Faraday (p. 26) at the Royal Institution of Great Britain, from 1820 to 1850. The methods found application on a large scale when Siemens and Gramme devised practical methods of winding armatures. Great electric motors and dynamos finally were constructed since 1870. In these powerful machines, electric engineering applies the electrical science of Oersted, Ampère and Faraday, and permits the economic transmission of power over a single wire to great distances.

## 35. QUALITATIVE ELECTROLYSIS.

1. Within a month after Volta had, by letter to the president of the Royal Society of London, described his fertile invention, two English chemists, Nicholson and Carlisle, succeeded in decomposing water by the current of the voltaic pile. This was the first step into ELECTRO-CHEMISTRY.

2. The Hofmann (p. 34) DECOMPOSING CELL in use at lectures consists of three communicating vertical tubes. The middle one has a globular reservoir at the top. The two lateral tubes are provided with a glass stop-cock at the top and with platinum ELECTRODES near the lower part. These electrodes consist of a rectangular piece of platinum foil, soldered to a platinum wire, which is fused through the glass.

3. When the apparatus is filled with dilute sulphuric acid—pure water is not a conductor—and the electrodes are connected with the conducting copper wires leading to the poles of the battery, bubbles of gas form immediately and rise to the top in a constant stream. The volume of the one gas is seen to be twice that of the other.

4. Very carefully opening the stop-cock over the larger volume, the issuing gas can be lit; it burns with a pale, hot flame; it is hydrogen. The other gas rekindles a glowing shaving; it is oxygen. Careful experiments have shown that none of the acid disappears. Accordingly, the galvanic current has decomposed water into its constituents, oxygen and hydrogen. Their ratio of volume is seen to be one to two.

5. Tracing the connections made by wire between the poles of the battery and the electrodes, it is readily seen that the current of hydrogen in the decomposing cell flows in the same direction as in the battery, namely from the zinc through the acid to the other solid in each battery cell. This is also the direction assumed by physicists for the current of positive electricity.



6. Accordingly, the entire circuit, comprising all the cells of the battery, the connecting metallic conductors and the decomposing cell, is pervaded by one continuous electric current flowing in the same direction. Produced in the battery cells by chemical action, directed from the zinc to the carbon, it flows in the same direction through the wire to the decomposing cell, accomplishes its chemical work and continues to its origin. Breaking the circuit at any point, the entire current stops throughout.

7. Before we can go on with this subject, we must make ourselves familiar with the necessary terms in use. The last carbon of the battery is called its **POSITIVE POLE**; the wire conductor connecting it with one of the plates of the decomposing cell makes this plate the **POSITIVE ELECTRODE**. The other pole and electrode are called the **NEGATIVE**. Now, bodies charged with unlike electricities attract each other, but when charged with like electricities they repel each other. Supposing the hydrogen drawn to the negative electrode, or pushed from the positive electrode, it has been thought to be or have been charged with positive electricity. At any rate, a substance appearing, like hydrogen, at the negative electrode, is **CALLED THE ELECTRO-POSITIVE CONSTITUENT** of the substance decomposed. See black-board diagrams.

8. The chemical decomposition effected by the galvanic current is called **ELECTROLYSIS**. The substance decomposed is called the **ELECTROLYTE**. The constituents collecting at the electrodes are called the **IONS**. Faraday called the electro positive ion, collecting at the negative electrode or **CATHODE** the **cathion**. The electro-negative constituent appearing at the positive electrode or **ANODE**, he called the **anion**.

9. For more careful experiments on electrolysis attended with the evolution of gases, it is advisable to use simple gas-collecting electrodes of the following form. The platinum wire is fused into a glass tube by means of which it is

fastened in a good cork or rubber stopper. This stopper also is provided with a small tube, connected with rubber to carry the gas to a gas burette or the pneumatic trough. The stopper is inserted in a suitable tube, placed into the electrolyte of a stand cylinder. If two such collectors are used, both gases can be collected separately.

10. If only liquids or solids are to be collected, a U-tube answers as decomposing cell, and platinum electrodes can be inserted from the top.

Using a blue vitriol solution, copper deposits as the negative electrode (the cathode). Make this the anode (positive electrode) and the copper dissolves again. Thus copper—and other metals—are the electro-positive constituent of metallic salts, and metals are dissolved at the positive electrode.

11. The solution of a neutral salt, like potassium sulphate, tinged ruby-red with cochineal, subjected to electrolysis in a U-tube cell, promptly shows a purple tint at the negative and an orange tint at the positive electrode. Consequently the acid is the electro-negative constituent of neutral salts, while the hydrate is the electro-positive constituent thereof.

12. Accordingly, SALTS ARE REALLY DUAL COMPOUNDS, as first concluded from the solution of the metals in acids, and as it is expressed in the chemical names of salts (for example, copper sulphate).

The electro-positive constituent (cation), appearing at the negative electrode (cathode) is hydrogen, metal or base.

The electro-negative constituent (anion), appearing at the positive electrode (anode) is oxygen, the acid radical or acid.

By secondary (simple chemical) reaction, the radical with water gives oxygen set free and the acid. Thus  $\text{Cu Sate}$  gives a deposit of Cu on the negative electrode, while the radical Sate, appearing at the positive electrode, must decompose the water, uniting with H to form the acid  $\text{H Sate}$ , setting free the O gas.

## 36. APPLIED ELECTROLYSIS.

1. The synopsis of facts presented in the preceding two lectures barely indicates the importance of the galvanic current to chemistry. In this lecture a few of the most instructive special scientific and technical applications of electrolysis will be added from the great number already in common use, and often grouped in special treatises on Electro-Chemistry.

2. Lavoisier had recognized lime, magnesia, potassa and

soda as bodies chemically resembling metallic calxes. Chemists had accordingly tried to produce such metals from them. Subjecting solid caustic potassa to electrolysis, HUMPHRY DAVY, at the Royal Institution, noticed the separation of minute white, metallic globules, burning almost as soon as formed. Thus the light metals (K, Na, Mg, Ca, Sr, Ba, etc.,) were first produced in 1807.



HUMPHRY DAVY.

3. The finely pulverized mineral fluorite (11, 10) treated with rather concentrated sulphuric acid in a covered dish of lead gives a most poisonous gas, which is an acid and has the special property of dissolving silica. It is used to etch glass where not protected by a film of wax. The supposed non-metallic or electro-negative constituent of this acid was called FLOURINE after the mineral, which itself, was called calcium fluoride, while the acid was called hydrogen fluoride.

4. All attempts to produce this hypothetical substance fluorine failed until 1886, when MOISSAN (p. 36) at the School of Pharmacy of Paris, succeeded in isolating and confining this

the most active of all substances. He obtained it by the electrolysis of the absolute (anhydrous) acid, in which anhydrous potassium fluoride had been dissolved to make the liquid a conductor. The decomposing cell had to be made of platinum, closed by stoppers of transparent fluorspar. The liquid was cooled to 50 below freezing.

5. FLUORINE appeared as a greenish yellow gas; liquefying at 95 degs. below freezing. It combines with mercury at common temperatures, and with iron or even platinum at a moderate heat. Iodine, sulphur, phosphorus, arsenic and carbon burst into flame in fluorine. Hydrogen and fluorine unite even in the dark with explosion. Fluorine decomposes water instantly, giving ozone and hydrofluoric acid. Hence the necessity of removing all traces of water to isolate fluorine.

6. Fluorine is the most strongly electro-negative substance known, precisely as potassium is the most electro-positive. Both have been first produced by electrolysis. Both decompose water at common temperatures. The metal potassium takes the place of the hydrogen, while the non-metal fluorine takes the place of the oxygen, by substitution.

7. While the isolation of fluorine cannot be exhibited to a class, it is very instructive to prepare and exhibit the corresponding non-metallic constituent of muriatic acid. The two cases are every way parallel. The liquid used is a saturated solution of salt with one-tenth its volume of concentrated muriatic acid. Electrodes of carbon have to be used, this gas readily attacking platinum at common temperatures.

8. The poisonous gas must be confined in a series of absorption flasks, Drechslers and columns. To avoid any gas escaping into the air, the last column should be charged with pumice wet with a strong solution of caustic potash. In a dish, aqua ammonia should be handy to remove the gas that may escape when substances are introduced into the glass vessels.

9. The gas produced at the positive electrode is yellowish green—hence it has been called CHLORINE by Davy, 1810.

It bleaches and destroys organic colors; it explodes with hydrogen; pulverized metallic antimony thrown into a cylinder with chlorine burns brightly. Potassium bursts into flame in chlorine. Its tendency to combine with hydrogen makes it destructive to organic tissue.

Chlorine is largely absorbed by water, forming chlorine water. This possesses the bleaching effects of the gas, and dissolves even gold and platinum in the cold to chlorides (19, 5).

10. Scheele first produced this gas (1774) by warming pyrolusite (9.7) with muriatic acid; he called it PHLOGISTICATED MURIATIC ACID. When oxygen had been recognized, Berthollet called it OXYGENATED MURIATIC ACID (1785). Lavoisier had supposed oxygen to be essential to all acids, as implied by the name: acid producer. Davy proved (1808) that muriatic acid contains no oxygen, but consists of the two substances hydrogen and CHLORINE only. Consequently MURIATES ARE CHLORIDES; and the equivalent of chlorine therefore is 35.5. See 27, 10.

11. By the method of Scheele, chlorine gas is produced on a large scale. Absorbed by lime and dilute cold alkalies, the so-called HYPOCHLORITES result (Ca, bleaching powder; Ka, eau de Javelle; Na, Labarraque's liquid). These are effective bleaching and disinfecting compounds. A warm concentrated solution of caustic potassa yields crystals of POTASSIUM CHLORATE (30, 8). The residue left after heating this salt to obtain oxygen, crystallizes in cubes from its solution; it is POTASSIUM CHLORIDE.—These compounds can all be obtained by the electrolysis of potassium chloride.

12. Electrolysis has long been applied in the arts for electroplating (gold, silver), electrotyping (Cu) and even in the metallurgy of copper and gold. Since the dynamo furnishes a cheap and powerful electrical current, chemical manufacturing is changing to a considerable extent, by the substitution of electrolytical for purely chemical processes. We shall come back to this subject later on.

## 37. EQUIVALENT AND ELECTRICITY.

1. In electrolysis we have a decomposition of a compound into its constituents without the addition of special reagents, excepting the presence of a volatile acid or the results of secondary reactions. Accordingly, electrolysis may be expected to furnish QUANTITATIVE METHODS OF HIGH PRECISION for the determination of many substances. Experience has fully confirmed this expectation.

2. Not only the most accurate, but at the same time the most RAPID DETERMINATION of nearly all metals, is effected by electrolysis. The substance is weighed in a PLATINUM DISH and dissolved therein. The dish is made the negative electrode, and the current kept up till no longer a trace of the metal can be detected in a drop of the solution. Then the solution is poured off, the metal generally adhering to the dish, is washed with water, then with alcohol; finally it is dried and weighed, still on the dish.

3. NO TRANSFERS having been made, a number of serious errors affecting all other analytical processes, are avoided in electrolysis. The solutions most serviceable are nitrates, sulphates and cyanides, exemplified in silver, copper and gold determinations. The degree of temperature, and the density of the current (amount per square centimeter of negative electrode) are of influence on the results.

4. Even if more than one metal be present, electrolytic determinations of each, in the same sample, are generally possible; for the tension required for the separation of metals in electrolysis varies considerably, and the acid or solvent used is of great influence. Thus copper is deposited by much less electrical tension than nickel. The investigations of Professor Edgar F. Smith, of Philadelphia, have been successfully centered on this practically important field; his special methods are advantageously followed in the laboratories.

5. STRIKING EFFECTS OF GALVANIC ACTION, have, however, long been used IN QUALITATIVE ANALYSIS. Thus,

metallic zinc reduces all the metals of the arsenic group; antimony and tin separate often in crystal form, arsenic largely escapes as gaseous hydrides, if sulphuric acid is used. The solutions are supposed to be contained in a watch glass, to permit examination by magnifier or microscope.

But if instead of a watch glass, the cover of a platinum crucible be used to contain the acidified liquid, galvanic action sets in. The current in the cell will go from the zinc through the acid to the platinum; hence the bubbles of hydrogen gas will appear at the platinum only. If antimony, even a bare trace, be present, it will go with the current, STAINING THE PLATINUM BLACK (or brown if exceedingly little be present). Neither tin nor arsenic stains the platinum. The tin deposits on the zinc. The arsenic largely escapes, as stated.

6. By connecting a pair of gas-collecting electrodes (35, 9) each with a gas burette, while the electrodes are placed in water, acidified with sulphuric acid, the hydrogen and oxygen gas can be most accurately measured. The volume of the hydrogen will, at every instant, be twice that of the oxygen. But direct weighings have shown oxygen to weigh 16 times as much as an equal volume of hydrogen (3, 12). Hence the weights obtained are as 16 to 2 or 8 to 1. Electrolysis gives the equivalent of oxygen 8, as found before by direct chemical means (31, 3-5).

7. If a strong current is used, the volume of oxygen gas possesses a marked odor and is less than half that of hydrogen. It has been found, that a portion of the oxygen has been condensed, its density being increased 50 per cent. This condensed oxygen is called OZONE. It is very much more active than ordinary oxygen. It decomposes potassium iodide, which oxygen does not do.

For these reasons it is best to measure the hydrogen only for quantitative purposes.

8. Since the hydrogen passes over continuously, its volume at any given time is a measure of the total electrical current used up to that time. Instruments for the measurement of

the galvanic current by the chemical effect produced are called **VOLTAMETERS**. The unit used is called the Ampère; it corresponds to 6 mgr. hydrogen in ten minutes time, or to 7.2 cc hydrogen gas per minute at common temperatures and pressure (i. e. when one mgr-Mg yields one cc hydrogen gas).

9. If a number of decomposing cells of the same kind, say charged with the same acidified water, be inserted in series in the same circuit, the electrolysis in all will not only be the same in kind or quality, but also the same in amount quantitatively. This equality remains, independent of any difference in form, magnitude or character of the different decomposing cells, placed in the same circuit. This proves, that **THE INTENSITY OF A GALVANIC CURRENT IS THE SAME AT ALL POINTS OF THE CIRCUIT**. This fact is really assumed in the use of the voltameter.

10. If the different cells, inserted in series in the same circuit, contain different compounds, the **ELECTROLYSIS SEPARATES CHEMICALLY EQUIVALENT AMOUNTS IN THE DIFFERENT CELLS** in the same time. Thus, acidified water, a copper solution, and a silver solution, connected in continuous series, yield qualitatively, at the negative electrodes, the positive constituents: hydrogen, copper and silver. Reducing the volume of hydrogen to weight, the proportions are invariably as 1 : 31.75 : 108, that is, as the equivalents of H, Cu, Ag. This is the electrolytic law of Faraday (p. 26).

11. A mercurous and a mercuric solution, placed in the same circuit, yield double the weight of mercury in the first. The equivalent of mercury in mercuric compounds has been found to be 100; in mercurous it is therefore 200. In a like manner, the equivalent of iron, in ferrous solutions, is known to be 28 (18, 10); but in feric solutions, it is only two-thirds thereof, or 18.66. The symbol for the —ous compounds has frequently been distinguished by small initial, thus hg 200, fe 18.66.



12. In this manner, the ELECTROLYTIC EQUIVALENT of many substances has already been determined by Faraday (1834); the value found was always the same as the CHEMICAL EQUIVALENT determined by chemists without use of electricity. Consequently, electrolysis takes place according to the proportions of the chemical equivalents. This is the LAW OF FARADAY. Fusible substances were also decomposed in the dry way, keeping them liquid by fusion. This avoids all secondary reactions caused by the presence of water (35, 12).

### 38. EQUIVALENT AND VOLUME.

1. Electrolysis shows that water contains two volumes of hydrogen gas for every one volume of oxygen gas (35, 3, 4). Evidently we may consider the two volumes of hydrogen gas chemically equivalent to one VOLUME of oxygen gas, precisely as we have called the corresponding WEIGHT one of hydrogen, chemically equivalent to the weight eight of oxygen.

2. But in doing so we would use the same term equivalent for relations of WEIGHT and of MEASURE (or volume). This slight imperfection of expression has been avoided, by speaking of volumes as HAVING A VALENCE (worth), while weights continue to be spoken of as BEING EQUIVALENT. Thus chemists say: 8 mgr. oxygen are equivalent to 1 mgr. hydrogen; and also: one volume of oxygen gas has the valence of two volumes of hydrogen gas.

3. If we adopt, for gases, the measure or volume as unit, and represent ONE volume by ONE symbol in roman type, (to distinguish it from the equivalent weights printed in italics), then the VOLUME FORMULA of water evidently becomes  $H_2O$ .

The equivalent formula *HO* is no less true, for it refers to equivalent WEIGHTS. Both formulæ express FACTS well

determined; in one case, they relate to weight, in the other, to gas measure (volume).

4. In the electrolysis of MURIATIC ACID, the gases produced can also readily be measured by our gas burette; we need only interpose our air lock, or any dry cylinder containing atmospheric air, between the decomposing cell and the burette. The chlorine will push the air into the burette, but not itself come in contact with the water.—The experiment shows the volume of the chlorine to be equal to that of the hydrogen. Chlorine therefore has the valence one. The volume formula of hydrogen chloride is  $\text{HCl}$ , the same as its equivalent formula,  $\text{HCl}$ .—After each experiment, the air lock must be properly ventilated.

5. AQUA AMMONIA can also be electrolysed. Most suitable is a concentrated solution of salt, to which not more than one-tenth its own volume of the strongest aqua ammonia has been added. Hydrogen will appear at the negative electrode, nitrogen at the positive electrode. The volume of hydrogen is exactly three times that of the nitrogen. That is, the valence of nitrogen is three, or one volume of nitrogen is equivalent to three volumes of hydrogen. The volume formula of ammonia is therefore  $\text{H}_3\text{N}$ . Its equivalent formula is  $\text{HN}$ .

6. The equivalent of nitrogen, by weight, has been found to be  $4\frac{2}{3}$ . That is, the weight of three volumes of hydrogen is to that of one volume of nitrogen as 1 to  $4\frac{2}{3}$ . Consequently, the weight of one volume of hydrogen is to that of one volume of nitrogen, as  $\frac{1}{3}$  to  $4\frac{2}{3}$ , or as 1 to 14. If the weight of one volume of hydrogen be taken as unit, one volume of nitrogen should weigh 14 such units. Actual experiments have shown such to be the case (3, 12).

7. It is true, all determinations made prior to 1895, gave 14.04; but as Lord Rayleigh has shown, this was due to the fact, that the presence of the heavier argon in the nitrogen had been overlooked (33.10). When making weighings with pure nitrogen, free from argon, Lord Rayleigh no longer found

14.04, but 14.00 as the weight of one volume of nitrogen. This, accordingly, is the volume weight of nitrogen.

8. In the same way, the volume weight of oxygen must be 16. For the two volumes of hydrogen gas, equivalent to one volume of oxygen, prove oxygen to be divalent. The equivalent weights 1 to 8 are as 2 to 16; hence one volume of oxygen gas should weigh 16, one of hydrogen gas weighing 1. Actual weighings have confirmed this conclusion.

9. For practical purposes the UNIT OF GAS VOLUME is that containing one milligramme of hydrogen; under common conditions of temperature and pressure, 12 cc. To determine this unit under any given conditions of pressure and temperature, find the volume occupied by the hydrogen gas generated from 12 mgr. pure magnesium. See 18, 9.

10. The valence of carbon cannot be determined directly, because carbon is not known as a gas. But fixed air contains 8 oxygen to 3 carbon (31, 7); or two equivalents of oxygen to one equivalent of carbon weighing 6 (31, 8). But direct experiments show, that when carbon is burnt in oxygen, the gas volume does not change. Since now one volume of oxygen is equivalent to two volumes of hydrogen, carbon must have the valence 4. All the numerous compounds of carbon confirm this conclusion.

11. THE VALENCE of a gas is the number of volumes of hydrogen chemically equivalent to one volume of the gas. By electrolysis we have found chlorine to be monovalent, oxygen divalent and nitrogen trivalent; that is, these gases have respectively the valence 1, 2, 3. By reasoning and calculation, carbon is tetravalent. All of organic chemistry will confirm this conclusion.

12. If three decomposing cells, charged with muriatic acid, water, and ammonia, are inserted in series in the circuit of a battery—say of eight Bunsens—the hydrogen gas, at the negative electrodes, will always be of exactly the same volume

in all three decomposing cells, in accordance with the general law of Faraday (36, 9, 10). At the positive electrode, the volume of chlorine will be equal to that of the hydrogen; the volume of oxygen will be half, that of nitrogen one third the volume of hydrogen. This form of experiment, due to Hofmann (p. 34) strikingly shows that Cl, O and N have the valence 1, 2, 3.

---

NOTES 8. Such gas weighings, for the purpose of verifying the data given, are readily made, without the use of air pump, by taking the hydrogen filled tube as standard of comparison.

I use a U-tube with side tubes and perforated ground glass stopper, of capacity 50 to 100 cc, and with fine wire for suspension to balance; weigh to tenth milligramme. For each gas to be weighed, a Kipp generator is used, but only one set of absorption and drying tubes, as slow but complete displacement is required anyway.

First, fill tube with pure, dry hydrogen and weigh; say the weight is  $a$ . Then connect with oxygen-Kipp, and weigh again; say it is  $b$ . Also fill with fixed air; let weight be  $c$ . Evidently  $b-a$  is the weight of oxygen over hydrogen, proportional to  $16-1=15$ ; and in the same way  $c-a$  is proportional to  $22-1=21$ . That is, the experiment must show the difference  $c-a$ , divided by the difference  $b-a$  to be equal to 21 divided by 15, which is 1.40. Actual experiment will show this to be the case, very nearly, and thus verify the statement, made in the lecture. It is evident that  $c-a$  divided by 21 should be very nearly equal to  $b-a$  divided by 15; for both quotients represent the weight of the dry hydrogen gas filling the weighing tube. This checks the accuracy of the work done.

Finally, if at the same time a determination of the unit volume, (approximately 12 cc) has been made, while the weighings were going on (see section 9), and if the capacity in cc of the weighing tube has been ascertained beforehand by weighing it with air and with water, the weight of the unit volume of hydrogen gas will be determined by dividing that unit volume into the volume of the weighing tube, giving the NUMBER of unit volumes handled; dividing this number into the weight of hydrogen filling the tube, as just determined, will give the weight of a unit volume of hydrogen gas. This should be equal to one.

Since hydrogen gas escapes readily, even during a weighing, and as all other gases replacing it are heavier, the weight is likely to be found a trifle above one. Morley's results.

## 39. EQUIVALENT AND HEAT.

1. The determination of the volume of substances by the method just described, is palpably restricted to gaseous bodies; to the much larger class of metals it is inapplicable. As has first been shown in 1819, by DULONG and PETIT, a determination of the specific heat of metals will establish this volume.

2. All amounts of heat are measured in gramme-degrees (25.11). The instrument used for such measurement is called a CALORIMETER. It consists of a metallic vessel, provided with stirrer and a sensitive thermometer; it is placed in another metallic vessel to minimize the loss of heat to the surroundings. Details of construction belong to laboratory practice.

3. Usually water is used as the HEAT MEASURING LIQUID. Suppose 100 cc water were used in the calorimeter; and suppose the temperature reads 20 degrees. If now 10 cc boiling water (of 100 degrees) be added, the temperature will rise to 27.3 degrees.

The 100 cc originally in the calorimeter rose 7.3 degrees, amounting to 730 gramme-degrees. The 10 cc were cooled from 100 to 27.3 degrees, or 72.7 degrees, giving off 727 gr° or practically as much as the 100 cc gained.

4. If, under the same circumstances, 100 grammes of sheet COPPER, in the form of bent cuttings, be rapidly transferred from a beaker with boiling water to the calorimeter charged with 100 cc water of 20 degrees, the temperature will also rise to very nearly 27.3 degrees. Hence, 100 gr. copper yield as much heat as 10 degrees water in the preceding experiment; or one gramme of copper carries no more heat per degree, than one-tenth of a gramme of water.

5. The amount of heat required to change the temperature of one gramme of any substance one degree (centigrade) is called the SPECIFIC HEAT of that substance. For copper it

has just been found to be 0.1, very nearly. Careful experiments, allowing for all influences, make it 0.094.

6. If we multiply the specific heat by the equivalent, we obtain the EQUIVALENT HEAT, that is, the amount of heat (in gr<sup>o</sup>) required to change the temperature of one gramme-equivalent one degree. The following table gives the determinations of specific heat, mainly by REGNAULT (1840).

7. TABLE of specific heat, equivalent weight (Eq.) and equivalent heat (Eq. H) of the principal metals.

Metal.	Sp.	Eq.	Eq. H.	Metal.	Sp.	Eq.	Eq. H.
Na. . . .	0.293	23	6.74	Cu. . . .	0.094	31.8	2.98
Mg. . . .	0.250	12	3.00	Ag. . . .	0.057	108	6.16
Al. . . .	0.214	9	1.93	Cd. . . .	0.057	66	3.76
Ka. . . .	0.166	39	6.47	Hg. . . .	0.033	100	3.30
Fe. . . .	0.114	28	3.19	Au. . . .	0.032	66	2.11
Zn. . . .	0.096	32.5	3.13	Pb. . . .	0.031	104	3.22

8. Of these metals, sodium and potassium were, already by Berzelius, considered to be equivalent to hydrogen, or in our modern language, to be monovalent. Their equivalent heat is about 6.5. Silver comes the nearest. The mean of these three is 6.44. This, therefore, is the equivalent heat of metals having the VALENCE ONE.

9. The seven metals: Mg, Fe, Zn, Cu, Cd, Hg and Pb show equivalent heat a little above 3. The mean of all is 3.23. This is evidently half the value of the preceding group. Doubling 3.23 give 6.46, practically identical with the equivalent heat of the monovalent metals. Two equivalents must be taken to get the same heat capacity, 6.5.

10. The equivalent heat of Al and Au averages 2.02, very nearly one-third of that of the first group. The specific heat of three equivalents of these metals is 6.06. Gold and aluminium must, therefore, so far as heat is concerned, be taken in three equivalents.

11. The specific heat of carbon varies greatly with temperature and condition. For charcoal it is 0.241, for graphite 0.197 and for the diamond 0.147. No conclusion as to val-

ence should be drawn from these data, which simply illustrate the allotropic conditions of carbon. The specific heat of carbon rapidly increases with the temperature. At some temperature it is concordant with the other substances. See 42 and compare 38.10. The specific heat of S, 0.177 and Io, 0.054. with the equivalents 16 and 127 give 2.83 and 6.86. Hence, S is divalent, Io monovalent.

12. For the gases H, N, O, the specific heat has been found 3.41, 0.244 and 0.218. The equivalents being 1,  $4\frac{1}{2}$  and 8, the equivalent heats are 3.41, 1.14 and 1.74. This agrees with the valence as determined by electrolysis. 1, 3, 2, yielding 3.41, 3.42 and 3.48 respectively for 1, 3, and 2 volumes.

Thus the valence of metals and non-metals is concordantly determined by volume and by specific heat.

## 40. ATOMS AND MOLECULES..

1. The solution of metals showed that certain definite WEIGHTS of the different metals are chemically equivalent. One hydrogen was found equivalent to 12 magnesium, 28 iron and 100 mercury. In electrolysis it was found that equal quantities of electricity set free the same equivalent weights of metals.

2. But these equivalent weights are not of the same value in reference to heating and space-occupying capacity; still, they differed in simple ratios, requiring one, two, three or four equivalents to obtain the same heat capacity, or having the space-occupying capacity of 1, 2, 3, 4 equivalents of hydrogen gas.—Here we have exclusively FIXED, SIMPLE MULTIPLE PROPORTIONS.

3. Neither equivalent alone, nor valence alone, fully characterizes any given kind of matter, such as H, O, N, C or Ka, Mg, Al, Si; both are required and expressed in the higher chemical unit, the ATOM.

AN ATOM IS A RELATIVELY INDIVISIBLE PARTICLE OF MATTER. It possesses a definite number of valencies, acting

like single EQUIVALENTS. That is, the atomic weight is equal to the product of its valence into its equivalent weight.

4. Hydrogen is the chemical unit, being the smallest. Its equivalent is one, its valence is one; hence also its atomic weight is one.

Oxygen has a valence two, and its equivalent is 8; therefore its atomic weight is 16. Nitrogen has a valence 3, its equivalent is  $4\frac{2}{3}$ ; hence its atomic weight is 14. Carbon has the valence 4, the true equivalent 3, the atomic weight 12.

5. The product of equivalent into specific heat for Ka, Na, Ag was 6.4 (39.8); their valence is one, and therefore their atomic weight the same as their equivalent weight. For the magnesium group (39.9), the corresponding product has to be doubled, hence the valence is 2, and the atomic weight twice their equivalent weight. For aluminium and gold (39.10) the product has to be trebled to make it equal to 6.4; hence the valence is 3, and the atomic weight three times the equivalent. For carbon the valence is 4.

6. In this manner we obtain the following preliminary table of atomic weights, arranging the metals vertically according to their electro-chemical character first, their valence next, and in each line according to the magnitude of their atomic weight. The metals in each line form a group or GENUS, designated by name and Greek symbol, essentially as in my *Atomechanics* of 1867.

Since carbon forms the natural center of this group, we shall call this the carbon system of metals—the metals predominating in number.

#### 7. THE CARBON-SYSTEM OF VOLATILE METALS, giving incrustation on charcoal.

Electro.	Val.	Name.	Sym.	1st.	2nd.	3rd.	4th.	5th.
POSITIVE,	1.	Kaloids,	Ka	Li 7	Na 27	.....	.....	.....
	2.	Cadmoids,	Kδ	Be 9	Mg 24	Zn 65.5	Cd 112	Hg 200
	3.	Styptoids,	Σr	Bo 11	Al 27	Ga 70	In 114	Tl 204
NEUTRAL,	4.	Adamantoids,	Aδ	C 12	Si 28	Ge 73	Sn 118	Pb 207
	2.	Phosphoids,	Φ	N 14	P 31	As 75	Sb 120	Bi 208
	3.	Sulphoids,	Θ	O 16	S 32	Se 79	Te 124	.....
NEGATIVE,	1.	Chloroids,	X	Fl 19	Cl 35.5	Br 80	Io 127	.....



Secondary, lighter, earth-forming groups:

POSITIVE,	1. Kaloids,	Ka	.....	Ka 39	Rb 85	Cs 132
"	2. Calcoids,	Xa	.....	Ca 40	Sr 88	Ba 137

The kaloids are the most strongly electropositive, the chloroids the most strongly electronegative; the intermediate groups are electrically intermediate. Compare 36, 7.

8. A corresponding group of non-volatile metals, giving NO INCRUSTATION ON CHARCOAL and less plainly characterized in valence, may be called the IRON SYSTEM OF METALS. Increase of atomic weight increases the electropositive character (contrasting with carbon system).

MOST NEGATIVE,	Molybdoids,	Mλ	Va			
			Cr 52	Mo 96	Wo 185	
			Mn 55	.....	.....	
	Sideroids,	Σδ	Fe 56	Ru 104	Ir 193	
			Ni 58	.....	.....	
	Palladoids,	Πδ	Co 59	Pd 106	Pt 194	
POSITIVE,	Cuproids,	Kv	Cu 63.5	Ag 108	Au 197	

9. The atomic weights here given are used in the calculation of analyses and in the preparation of solutions and compounds. The terms milligramme-atom and gramme-atom are readily understood; a mgr.at. is the number of milligrammes equal to the atomic weight. Thus a mgr.at. of silver is 108 mgr. silver, and a gr.at. sulphur is 32 grammes of sulphur.

10. A MOLECULE is the smallest number of atoms forming a physical system, moving as a single body.

IN THE GASEOUS STATE, and under the same temperature and pressure, the molecular volume of all substances is the same (LAW OF AVOGADRO, 1811).

The practical unit of weight being the milligramme, the mgr. molecular volume of any substance in the gaseous state is the number of cc occupied by 2 mgr. of hydrogen gas.

11. This law gives a ready means for the DETERMINATION OF THE MOLECULAR WEIGHT of volatile substances by methods resembling specific gravity determinations. It is only necessary to determine the volume *v* in cc, occupied by a known weight, *w* mgr. Under the same conditions of temperature and pressure, 24 mgr. Mg. yield *q* cc hydrogen gas,

to be determined by direct experiment (38, 9). Hence the  $v$  cc gas represent  $v$  divided by  $q$  mgr. molecules; let this number be  $n$ . Then the weight  $w$ , is  $n$  mgr. molecules, each one molecule therefore weighs  $w$  divided by  $n$ .

12. Such determinations constitute an essential part of all laboratory work. It is carried out by means of my gas burettes, with or without air lock, and also by the Victor Meyer displacement apparatus.

Experiments show that, as for hydrogen, so for oxygen, nitrogen and chlorine, also for vapors of bromine and iodine, the molecule consists of two atoms. For water, carbon dioxide and other gases obtained by synthesis, the molecule consists of one atom only, such as  $H_2O$ ;  $CO_2$ .

NOTES. That chemical compounds differ from mixtures in having their constituents united in fixed, definite proportions, was more or less understood over a century ago. The investigations of WENZEL and especially RICHTER (p. 33) on neutral salts and the combining proportions of acids and bases, made this clear. It was however, drawn in question by no less a chemist than Berthollet (p. 32), but settled against him by PROUST.

DALTON (p. 32), comparing the different oxides of metals and a few gases as to composition, found that all facts known could be expressed by saying: SUBSTANCES COMBINE IN FIXED, SIMPLE MULTIPLE PROPORTIONS BY WEIGHT. Being a thinker, as well as a chemist, he conceived the idea of limited particles of matter, each kind having a definite weight of its own; such particles would combine only in fixed and simple multiple proportions. For the name of these particles he revived the term atom from the old Greek philosophers, who thereby designated the final, indivisible particles of matter.

Independent of all philosophical speculation, the chemical atom, as defined by us, is as real as matter itself. The chemical atom is RELATIVELY INDIVISIBLE, that is, in reference to the substance which is composed of these atoms. Atoms of water are indivisible as such; for if divided, water ceases to be constituted by them; we have only atoms of the constituent hydrogen and oxygen.

This idea of relative indivisibility is not restricted to chemistry, but is quite general. A book, a flower, an animal, also are as indivisible as the atom—in relation to the kind of being they are. In other words, the final philosophical question of the limited divisibility of matter in general is not part of the question of the reality of chemical atoms.

A certain prominent modern chemist denies the reality of chemical atoms—but he also denies the reality of matter. A chemist denying matter is exclusively a modern phenomenon.

## 41. ELEMENTS AND COMPOUNDS.

1. We have begun the study of chemistry proper with the study of THE METALS. This well defined and most important class of bodies also formed the starting point for the chemists of old. For about a century, this natural and to all familiar group of bodies, has been put into the back ground by chemists. We deliberately have begun our course in chemistry with the substance rather than with the shadow.

2. We have also noted a class of bodies called non-metals, comprising sulphur, carbon, iodine. To this group we afterwards added the noted gases hydrogen, oxygen, nitrogen and chlorine. These bodies combined with the metals, forming new bodies, chemical compounds. By heat, and notably by electricity, we have decomposed these compounds, reproducing the original metal at the negative electrode, and recognizing the non-metals as electro-negative substances.

3. Looking at the grouping of the metals in 40, 7 and 8, we are struck with the MANY RELATIONSHIPS brought to our mind in tracing the lines from right to left, following the species of a genus with increasing atomic weight, or up and down, according to varying valence and electrical contrast. They look not at all like independent substances, but rather like compound bodies, systematically arranged according to their composition.

4. Nevertheless chemists, the world over, have considered these bodies to be simple substances, not compound. Modern chemists have derided their predecessors of two thousand years, who looked upon the metals as compounds, the alchemists even deliberately trying to change one metal into another. Are the chemists right and were the old chemists in error? Let us examine the facts without prejudice.

5. The principal means of decomposition at hand are increase in temperature and electrical tension and current. We

have exemplified the use of both these powers. Thus far, the metals have resisted both of these powers under all conditions. They clearly form a class of matter different from ordinary compounds, which we have decomposed. Hence, they ought to be designated by a distinctive name. We properly adopt their common name **CHEMICAL ELEMENTS**. The non-metallic elements are commonly called **METALLOIDS**.

6. But the definition of this term should be in accordance with fact. A **CHEMICAL ELEMENT IS A SUBSTANCE THAT HAS NOT BEEN DECOMPOSED**. To say that it **CANNOT** be decomposed would be to assert that those who succeed us will be limited by our powers and our knowledge. Such assertions are manifestly unwarranted and unscientific. History has often proved them to be false.

7. As to volume in the gaseous state, the elements deport themselves exactly as compounds. The molecular volume is the same for all. There is no difference whatever in this most fundamental relation between the elements and compounds.

8. As to specific heat there is a radical difference. Berthelot has first recognized and formulated it (1873). The specific heat of an atom of any chemical element is the same (39), entirely independent of the weight of that atom, though this weight varies from 1 to over 200! But for a series of compounds, resembling one another, the specific heat of the compound atom is almost directly proportional to the atomic weight.

9. I have shown that there is also a radical difference between the effect of the **SUBSTITUTION** of an element and a compound on the properties produced (1892). In certain simple organic compounds called **PARAFFINS**, one hydrogen atom may be replaced by an atom of **Fl**, **Cl**, **Br**, **I** or **Cyanogen**, which is **Cy = CN**, a compound radical of the atomic weight 26. The boiling point increases with the atomic weight of the elements in these substitutions, as shown in

the diagram, page 77. Here Cy is at the top, showing the greatest increase, more than for  $lo=127$ ; in fact, for an element it would require an atomic weight of 150. Yet the radical has only the atomic weight 26.

10 Both of these striking differences between elements and compounds were fully accounted for on mechanical principles in my notes presented by Berthelot to the Academy of Sciences of Paris (1892). The conclusion is not, that the elements are really simple bodies, but that the constituent particles of their atoms are at relatively small distances, as compared to the relatively great distances of the element atoms in ordinary compounds.

11. Thus the question as to the simple or composite nature of the chemical element stands in the following position. No chemical element has thus far been actually decomposed; the observations of Lockyer (1879) and Crookes do not warrant the conclusion drawn by these scientists. But at the same time, not a single fact is known proving or indicating that the elements are not composite substances; on the contrary, their mutual relationship, exhibited in the tables (40, 7, 8). showing their properties to vary with weight and valences, is a positive indication of their being compounds.

12. The pretended exact atomic weights of Stas (p. 33) are commonly considered to prove that the elements cannot be compound bodies; but these data have been shown to be erroneous in my communications to the Academy of Sciences of Paris and in my *True Atomic Weights*, 1894. The values of Stas are not constant, but vary with the amount of substance used. See p. 79. In this work, the so-called "Periodic Law" of the common text books is also examined.

The first extended publication on the natural classification and composite nature of the elements was made in my *Programme of Atomechanics*, 1867.

## 42. ALLOTROPY AND ISOMERY.

1. The three substances charcoal, graphite and the diamond, have been known to man from very early times. They are as different from one another as any other three bodies possibly could be. No chemist suspected these bodies to be related in any way, until in modern times. The transparent and most valuable gem (10, 12), the marking substance of our pencils, and the charred remains of wood, seemed to be bodies entirely unrelated.

2. Nevertheless, these three bodies are not only related, but they are chemically one and the same element carbon, in three different (ALLOTROPIC) states or conditions. Berzelius coined the word used; it explains nothing, only fixes in our mind, by a special term, a special set of facts. Other elements, especially S, P, O also show allotropy.

3. The following properties are common to all forms of carbon, and thus characterize the SPECIES of matter chemists designate by the symbol C : Solid, infusible and non-volatile in the highest heat of our furnaces, but volatilizing (boiling?) in the electric arch; combustible, at least in pure oxygen, at a red heat, yielding eleven-thirds of its own weight of carbon dioxide gas and nothing else; it is insoluble in all ordinary solvents, but dissolves readily at the highest temperatures (electric furnace) in many molten metals.

4. That even the DIAMOND IS COMBUSTIBLE, was first suspected by Newton (1740), because of its high refractive power. The combustion of the diamond was first effected in oxygen by Lavoisier, who thus established its true chemical nature. The TEMPERATURE OF IGNITION varies greatly with the form of carbon. Certain charcoals, made of willow wood at low heat, ignite at correspondingly low temperatures and are used for gunpowder. Graphite and diamond do not burn even in oxygen until at a bright red heat.

5. CARBON DISSOLVED in molten iron (cast iron contains 5 per cent.) may crystallize on cooling. This form is invariably GRAPHITE, soft, readily marking paper and wood (pencils), G 2.2 and rhombohedral. When such a carbon solution in iron is suddenly chilled on the surface, to solidification, the interior is compressed by the shrinking of the solid crust, and the carbon crystallizes, under this high pressure, as DIAMOND (Moissan).

6. The various common forms or VARIETIES OF CARBON, both mineral and artificial, have been sufficiently indicated. See 5, 2.3; 10, 12; 12, 10. Bituminous coals, when heated in a retort or oven, leave a COKE, corresponding to the charcoal left by wood under like conditions. Resinous substances yield lamp black, the lightest form of carbon. Bones give animal charcoal, the noted absorbent for color and other matters. The volatile portion of bituminous coals, purified, is illuminating gas.

7. PHOSPHORUS also presents itself in two allotropic conditions, namely ordinary amber colored and red phosphorus. By keeping ordinary phosphorus heated to 240 degrees for ten days continuously, it is converted into the red modification. To remove the small parts of the common (poisonous) phosphorus from the red (non-poisonous) modification, the cold mass is treated with bisulphide of carbon, which dissolves the common and not at all the red phosphorus.

8. The following additional contrasting properties are worthy of notice. The property first given applies to common phosphorus; the corresponding property of the red modification is put into parenthesis.

Specific gravity, 1.83 (1.96). Phosphorescent on surface (not). Inflammable at 60 degrees (230 degrees). Violently attacked by nitric acid (only slightly attacked when heated), making this a dangerous reaction (comparatively safe). Crystallizes at common temperatures (at 580 degrees).

9. SULPHUR also exhibits allotropic modifications. Its dimorphism has been fully presented (21, 6.7). When limpid

melted sulphur (113 to 120 degrees) is heated to about 200 degrees, it becomes viscid; above that temperature it again becomes a limpid liquid. The viscid sulphur (at 230) poured into water, stays soft for a long time, and is used for taking molds.

10. OXYGEN GAS under the influence of electrical discharges—even in electrolysis (37.7)—changes to ozone, the more active form of oxygen. Silver is not attacked at common temperatures by pure, dry oxygen; ozone promptly blackens it. The density of ozone is 50 per cent. in excess of that of oxygen; that is, while oxygen gas has the molecules  $O_2$ , those of ozone are  $O_3$ . Ozone readily reverts to oxygen; a moderate heating is sufficient for this change.

11. A chemical compound existing in two or more physically different forms is called ISOMERIC. Thus mercuric iodide shows two isomeric forms, the red and the yellow (23, 7.8). Mercuric sulphide, precipitated from its solutions by hydrogen sulphide, is black (22, 8 and notes). By heating, this black sulphide changes to a red sublimate, cinnabar. White arsenic crystallizes on a hot surface prismatic, on a cold surface octahedral; on a very hot surface it condenses to a vitreous mass, which gradually turns opaque like porcelain.

12. The phenomena of allotropy and isomery must evidently be carefully considered when the nature of the elements is to be investigated. Dimorphism may be looked upon as the expression of two positions of equilibrium, as already demonstrated in my programme of 1867. Allotropy is probably also dependent on the formation of more complex molecules, by the grouping of more atoms, as is plainly proved in the case of oxygen and ozone.



## 43. BINARIES AND TERNARIES.

1. Two elements combining, form a binary compound; three elements united, form a ternary compound. But nearly all compounds being DUAL, as we have seen quite early in the course, and as has been confirmed by electrolysis, we more properly look upon compounds as containing TWO constituents only, one or both of which may be compound radicals. Lect. 31.

2. The electropositive constituent of a compound is a metal (in salts) or hydrogen (in acids); the metal and hydrogen being interchangeable by substitution. If therefore, the FORMULA OF THE ACID be given or remembered, it is easy to state the formula of the corresponding salt, provided the valence of the metal be known. Substitution taking place, not atom for atom, but equivalent (i. e. unit of valence) for equivalent.

3. For example, the formula of hydrochloric acid or HYDROGEN CHLORIDE is  $\text{H Cl}$ ; both constituents being monovalent, the atomic and equivalent formula are identical. Now Ag being monovalent, Ag Cl<sup>ide</sup> will be expressed by the formula  $\text{Ag Cl}$ . But zinc is divalent, hence its chloride has the formula  $\text{Zn Cl}_2$ . Bismuth being trivalent, its chloride is represented by the formula  $\text{Bi Cl}_3$ . The number of monovalent negatives must equal the valence of the positive constituent.

4. If now instead of Cl we have any other chloroid, the formula will remain the same, only the second symbol will change. Thus silver fluoride  $\text{Ag Fl}$ . Zinc bromide  $\text{Zn Br}_2$ . Bismuth iodide  $\text{Bi I}_3$ . These are all binaries proper. Even the radical cyanogen, Cy or CN gives compounds of this structure and named like a binary, cyanide. Thus  $\text{K Cy}$  represents potassium cyanide,  $\text{Ba Cy}_2$  barium cyanide.

5. If instead of starting with hydrogen chloride, we start with NITRIC ACID,  $\text{H N}^{\text{ate}}$ , the formula of which is  $\text{H O}_3\text{N}$ , we still can write the formula as before, for NITRATES ARE DUAL COMPOUNDS, CONTAINING THE MONOVALENT RADICAL

$O_3N$  AS ELECTRO NEGATIVE. Thus silver nitrate has the formula  $Ag\ O_3N$ ; barium nitrate  $Ba\ (O_3N)_2$ , bismuth nitrate  $Bi\ (O_3N)_3$ .

Chlorates correspond exactly to nitrates. Thus  $KaClate$  has the formula  $Ka\ O_3Cl$ ;  $BaClate$  is  $Ba\ (O_3Cl)_2$ .

6. OXIDES are binaries containing the divalent electro-negative ELEMENT oxygen. The formulæ  $H_2O$ ,  $Ba\ O$ ,  $Ka_2O$ ,  $Zn\ O$ ,  $CO_2$ ,  $Si\ O_2$  are perfectly normal, the valence of the negative balancing that of the positive constituent. For phosphoids, to avoid fractions, we write  $P_2O_3$ ; but this involves a question, which we must leave untouched at present.

Sulphides correspond exactly to oxides;  $Zn\ S$ ,  $C\ S_2$ ,  $Ba\ S$ .

7. SULPHATES correspond also to oxides, containing the DIVALENT RADICAL  $O_4S$  instead of oxygen; our Sate is  $=O_4S$ . Thus the formula of sulphuric acid is written  $H_2O_4S$ ;  $Ba\ Sate$  is  $Ba\ O_4S$ . Potassium sulphate  $Ka_2O_4S$ . Zinc sulphate  $Zn\ O_4S$ .

CHROMATES contains the divalent radical  $O_4Cr$ , SULPHITES the divalent radical  $O_3S$ . Consequently lead chromate is  $Pb\ O_4Cr$  and calcium sulphite  $Ca\ O_3S$ .

CARBONATES contain the divalent radical  $O_3C$ . Hence zinc carbonate  $Zn\ O_3C$ .

8. NITRIDES contain the trivalent element nitrogen as negative. The most important nitrides are those of the trivalent phosphoid group. For example, ammonia  $H_3N$ , phosphuretted hydrogen  $H_3P$ , arseniuretted hydrogen  $H_3As$ .

The nitrides of the chloroid group are all explosive. Thus  $N\ Cl_3$  is perhaps the most explosive of all substances.

9. PHOSPHATES, normal, contain the TRIVALENT RADICAL  $O_4P$ ; hence their formula may be written exactly as that of a nitride. The acid is  $H_3\ O_4P$ . Potassium phosphate  $Ka_3\ O_4P$ .

ARSENATES correspond to the phosphates.  $H_3\ O_4As$  is arsenic acid,  $Ag_3\ O_4P$  represents normal silver phosphate.

It is not necessary to give cases of tetravalence at this place. They will be understood when they occur.

10. It is evident that for example, in sulphates, the two hydrogen atoms of the acid need not both be replaced by a metal; in that case we obtain a so-called ACID SALT, commonly designated by the prefix bi—. Thus  $\text{H}_2 \text{O}_4\text{S}$ ,  $\text{HKaO}_4\text{S}$  and  $\text{Ka}_2 \text{O}_4\text{S}$  represent H Sate, Ka bisulphate and Ka Sate. The same terminology is applied to carbonates and sulphites. Thus  $\text{HKA O}_3\text{C}$  represents Ka bicarbonate, and  $\text{HNa O}_3\text{S}$  represents Na bisulphite.

11. For the TRIVALENT RADICALS, such as  $\text{O}_4\text{P}$  of phosphates, the three valencies  $\text{H}_3$  may be represented by  $\text{KaH}_2$ ,  $\text{Ka}_2\text{H}$  or  $\text{Ka}_3$ ; such salts are termed monopotassic, dipotassic and tripotassic phosphate. But also metals of other valence may enter. Thus the crystallized ammonio-magnesium phosphate, precipitated from alkaline solutions, is  $\overset{\text{Am}}{\text{Mg}} \text{O}_4\text{P} + 6 \text{H}_2\text{O}$ . The trivalent radical is saturated by the divalent Mg and the monovalent ammonium Am. In the so-called microcosmic salt, the three valencies are represented by one atom each of sodium, ammonium and hydrogen; the salt contains four atoms of water of crystallization. Write the formula.

12. These general rules and special examples may suffice for the understanding of the writing and reading of chemical formulæ. The common (now atomic) formulæ represent one atom of the compound. The positive is generally a metal or hydrogen. The electro-negative is an element (in binaries) or a radical (in ternaries). It is the valence, that is, the number of equivalents, that must balance in the formula as in the compound.

The more general group formulæ (Greek symbols of genera) given already in our *Atomechanik* 1867, can only be mentioned here. These general formulæ are also used in our treatise on the statistics of crystal symmetry in the transactions of the Academy of Sciences of Vienna for 1870.

---

NOTES. A practical difficulty in the writing of chemical formulæ must yet be cleared up. We may say, in general, that the metals also occur combined, forming radicals.

Thus mercury is considered divalent—in the mercuric series of compounds. But in mercurous compounds, we must consider TWO atoms of mercury combined to form the divalent radical  $\text{Hg}_2$ .

Again, ferrous compounds contain one atom of iron combined with only two valencies of the negative; it is said that ferrous compounds are NOT SATURATED. When oxidized to ferric, the iron radical  $\text{Fe}_2$  has formed, with a valence 6. Ferric chloride contains 2 Fe as positive and 6 Cl as negative. Ferric sulphate contains the hexvalent  $\text{Fe}_2$  saturating three divalent radicals  $\text{O}_4\text{S}$ .

In like manner, the tetravalent Pt forms two series of compounds, the PLATINIC and PLATINOUS. The first are considered normal, each Pt being combined with four equivalents (valencies) of the negative element or radical. In the platinous, each Pt is combined with two such valencies only; these compounds are spoken of as non-saturated.

In the same manner we have Stannous (non-saturated) and Stannic (saturated) compounds.

Fixed air, carbon dioxide, is considered saturated  $\text{CO}_2$ ; four valencies or equivalents of the positive carbon being united with two divalent oxygen atoms. But carbonic oxide is  $\text{CO}$ ; it is considered non-saturated, but acts quite like a neutral body.

These few remarks have been added only to deal with the practical points involved in the writing and reading of chemical formulæ, not to solve difficulties in valence.

CONSTITUTION OF TERNARIES. The author wishes it distinctly understood that ALL the detail given even in elementary text books on this subject is unreliable, useless and misleading; much thereof is in conflict with crystallographic facts now commonly disregarded. Deeming it improper, in a text book, to teach anything untrue and in conflict with fact, all elegant structural formulæ of ternaries are deliberately excluded from this work.

What has been given on their constitution is perhaps both new and old—new in not being found in the books of the day, and old in being conform to the representations of an earlier day; but it has two good reasons for a place in this text book, namely it is strictly conform to chemical and electrolytical phenomena, and does not go beyond the solid basis of experience.

NAME OF TERNARIES. The ending is in T, indicating THREE elements combined; the connecting vowel is A for common, I for a less amount of oxygen. In English, a final E is added to the T. Thus we have iron sulphate and sulphite.

The ternaries, with more oxygen than the ATE, take the prefix PER, those with less than ITES take HYPO before the negative. Thus perchlorates and hypochlorites.

If intermediate element of ternary be not oxygen (understood in preceding), then root of name must be inserted. Thus  $\text{K a S-Asite}$  is potas-

sium sulph-arsenite; Am Cl-Ptate, ammonium chloro-platinate. As intermediate occur mainly O, S; Fl, Cl, Br, Io, Cy. Yellow prussiate is Ka Cyo-Feate, red prussiate Ka Cyi-Feate; Cyo reads cyano—, and Cyi reads cyani.

## 44. FORMULA AND COMPOUND.

1. We have now exposed all the essential principles on which the MODERN CHEMICAL FORMULÆ are constructed. We have also given a sufficient number of examples to make the practice of writing such formulæ reasonably easy. We regret the necessity of words of warning against the almost universal ABUSE of these formula.

2. The student should always bear in mind, that the CHEMICAL FORMULA of a compound IS NOT THE COMPOUND itself. The name is not the thing. The word is not the object. And yet it is a fact, that in lecture halls and laboratories, in books and periodicals, the chemical formula is made much more prominent than the chemical substance, or its reactions and properties.

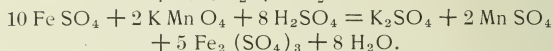
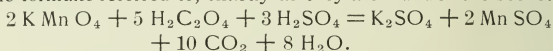
3. The chemical formula, if correct, is merely a symbolic representation of one atom of the chemical compound. Above all, it is applicable only to substances sufficiently pure, never to crude materials. To refer, by chemical formulæ, to crude acids and ordinary chemicals, is false in every sense of the word. Such a practice does not show learning, but proclaims ignorance.

4. To avoid such practice, we have from an early day used the simple abbreviation of the chemical names now familiar to the student. H Sate is more brief than the name hydrogen sulphate or sulphuric acid; it represents the actual DUAL nature of the compound which must be known to understand its reactions; it does not hide the chemical essence under a string of letters or symbols such as  $\text{H}_2\text{O}_4\text{S}$ .

5. Unless the radical is broken up in an exceptional reaction, it acts like one thing, like an element atom; and any expression hiding that fact, hides the mechanism of the chemical reaction, hides that which we try to teach or to learn. Besides, it does not put an undue strain on the memory, and thus gives the mind a chance to think of the essential clearly.

6. Again, intricate formulæ, supposed to represent reactions, are written on blackboards, and printed in books, for students to learn; and yet these formulæ are not true, and the reactions will not take place at all, if the materials are taken strictly conform to these formulæ. The chemical process learnedly represented will simply not proceed. Such are, for example, the long equations expressing the volumetric reactions of potassium permanganate with oxalic acid and ferrous salts.

7. As we shall not burden these pages with such formulæ ourselves, and as the lesson has to be brought home, we insert the formulæ referred to, exactly as they are found in the books.



Now, if you will take precisely these quantities, the reaction will not take place as expressed—the determination attempted will be a miserable failure. The only result is the bewildering of the student. The real mechanism of the simple chemical reaction is completely obscured by a cloud of irrelevant and false details.

8. PERMANGANATE,  $\text{K}_2\text{O}_4\text{Mn}$ , was first produced (1820) and applied by my teacher in chemistry, Professor Forchhammer of Copenhagen. In the presence of oxidable materials, AND A LARGE EXCESS OF SULPHURIC ACID, it breaks up, the Mn forming ordinary compounds as electro-positive. Now, the only and the essential thing to know, is that 2 permanganate will yield one  $\text{K}_2\text{O}$  and 2  $\text{MnO}$ , the excess of acid attends to keeping them in solution. But this

accounts for 3 of the 8 oxygen; hence 5 oxygen are set free to do the work wanted done.

9. The effect of this oxygen on the oxidable matter is equally simple. The ferrous  $\text{FeO}$  becomes ferric,  $\text{Fe}_2\text{O}_3$ ; or 2 ferrous require one oxygen to become ferric, which is kept in solution by the large excess of acid. The five oxygen from two permanganate will therefore oxidize ten ferrous; that is, ONE PERMANGANATE OXIDIZES FIVE FERROUS. This gives the numerical relation wanted. By the way, the long equation is still too short; green vitriol should have been replaced by hydrated ammonio-ferrous sulphate, which is the true standard. See the blackboard diagram.

10. The books should be freed of such useless, complex and incorrect show of chemical learning which only perplexes and misleads the student. For one, the author will no more introduce such sham chemistry in this textbook than he allows it in his laboratory. We endeavor to study the actual process in its essential and determining features, even if we lose the appearance of learning.

11. To give chemical formula, when asked to describe a chemical compound, is not giving an answer at all. The characteristic properties of the substance determine its nature, and not the formula. It is the substance we prepare, test and use, not the formula. The substance may cure disease, the formula can not do that. Compounds are not marked by nature with chemical formulæ, but by properties; it is by these that we have to distinguish them.

12. The abuse of formulæ is especially out of place at the laboratory stand in qualitative analysis. The chemists of the present have, under a new name it is true, returned to the dualistic Berzelian constitution of compounds, always retained by the author, and expressed in his simple signs. These two constituents determine the reactions; the complete formula only hides it from the eyes.

## 45. PURITY AND STRENGTH.

1. A chemical compound should be pure, that is, contain nothing but what its name implies and its formula indicates. But such absolute purity is almost impossible to procure; only for the most important atomic weight determinations is an effort made to reach this limit. Commercial products, even if marked C.P., are not absolutely pure.—See True Atomic Weights, p. 140-142.

2. Although it may be extremely difficult to secure the highest degree of purity, it is comparatively easy to prove the presence of the foreign matter or impurity. The general methods of QUALITATIVE CHEMICAL ANALYSIS (Lect. 22) form the basis of the tests for impurities; special tests of great delicacy are sought for in particular cases. We shall consider that subject soon.

3. Many chemicals it is impracticable to produce in the free state; they are sold as solutions in some inert solvent. This is the case with most acids and the volatile alkali, which are sold in aqueous solution. For this class of bodies, it is essential that nothing but the chemical and the inert solvent be present, and that the amount of the active substance be not below the per cent. stated. Here both purity and strength are required.

4. All methods for the determination of the strength of solutions and chemicals in general belong to QUANTITATIVE CHEMICAL ANALYSIS. The scientific principles involved are subjects proper for the lecture room, though the details of manipulation and the minutiae of method to secure most reliable results belong, with the practice, to the laboratory.

5. First of all, these quantitative methods may be distinguished as physical and chemical, according as mainly physical processes are employed, or the substance is submitted to chemical transformations by the use of reagents.



6. The PHYSICAL METHODS of determining the strength of a given chemical consist in the determination of the so-called PHYSICAL CONSTANTS of the substance, such as the specific gravity, G; the fusing point, F; the boiling point, B; also the refracting power; the rotation of the plane of polarization; the solubility in certain neutral solvents, and the like. The first three (G, F, B) are the most important.

7. There are two methods, depending exclusively on physical agencies, but accomplishing chemical changes in the given substance; namely dissociation and electrolysis. DISSOCIATION is chemical decomposition by heat alone; ELECTROLYSIS is chemical decomposition by the galvanic current. Both of these methods are capable of a high degree of precision; they are also rapid and simple in execution.

8. The CHEMICAL METHODS proper, involving the use of reagents and producing chemical transformations of the given substance, may be distinguished as gasometric, volumetric and gravimetric methods of quantitative analysis. The first named is the most recent and the most rapid, but unfortunately also the most restricted in applicability; the last named method is the oldest and the slowest, but applicable in all cases, and serves as standard of comparison for the others.

9. In GASOMETRIC ANALYSIS, the substance to be determined is acted upon by a reagent, setting free some gas; this gas is measured, and its amount is proportional to that of the compound to be determined. It is evident, that this reaction must be rapid and complete, and affect exclusively the substance to be determined. Gasometric analysis is entirely distinct from GAS ANALYSIS proper, which treats of the analysis (by absorbents) of mixtures of gases. Lect. 32.

10. In VOLUMETRIC ANALYSIS, the substance is brought into solution, and treated with some reagent of definite strength, called a NORMAL SOLUTION; this solution is added, finally drop by drop, until the reaction intended is completed, as INDICATED by some readily recognizable change in color

or appearance. The volume of normal solution used, then furnishes a measure of the strength of the substance.

11. In GRAVIMETRIC ANALYSIS, a weighed portion of the substance is, by appropriate reagents, transformed into some other definite combination, which can be readily and ACCURATELY WEIGHED. The weight so obtained, furnishes the measure of the strength sought. Thus, a silver coin dissolved in nitric acid, will give all its silver as precipitate, when a chloride is added; this precipitate washed, dried, fused and weighed, gives the weight of silver chloride; 0.7526 thereof is silver, which thus becomes known.

12. Whatever method be used, in all cases the real determination depends on one or more weighings. In volumetric processes, the reagents depend on weighings, and in all cases the substance taken must be weighed. Accordingly, THE BALANCE remains to-day, as it always has been, THE REAL INSTRUMENT OF QUANTITATIVE CHEMICAL ANALYSIS, in all its varied forms and under all names. And in all the operations of quantitative analysis, the chemical formulæ and atomic weights are the standards of comparison. This is the legitimate use of chemical formulæ.

## 46. THE ANALYTICAL BALANCE.

1. The exposition of the general methods of quantitative chemical analysis must begin with a short study of the analytical balance (2, 6) with AGATE BEARINGS. The handling of this instrument is more important than its first cost. The finest balance improperly handled, can give no reliable results, while a good prescription balance, in glass case, and well handled, gives results to 2 mgr. certain, and almost to the single milligramme.

2. In this lecture course we shall, as a rule, consider weighings to the milligramme only. These can be obtained by the method of equal excursions of the POINTER (2, 8) from the central line of the scale.

In actual laboratory practice, it is advisable to determine the scale value in milligrammes; then a simple mental calculation will give the true milligramme without frequent adjustment of the pointer.

3. The analytical balance is provided with a RIDER which can be moved to any division of the scale marked on the beam, while the case is closed. Of course, the balance must be arrested, as in every case of change of weights (2.8). By such a balance, even the simple method of equal excursions, will permit the determination of the tenth milligramme.

4. The balance should be PLACED on as firm and stable a support as can be found, in good light, but protected from the direct rays of the sun. The balance should be carefully leveled, by means of a spirit level (independent of the unsatisfactory box levels usually fastened to the balance). All necessary adjustments should be made and revised at reasonable intervals. Careful handling avoids frequent change of adjustment.

5. A good balance should be provided with a separate stop for the pans, in addition to the stop for the beam. Having weighed a burden on the left pan, the balance should come to the same equilibrium after exchanging the burden to the right and the weights to the left pan; this tests the EQUALITY OF THE LEVER ARMS (2.6).

All trepidations, all unnecessary motions of any kind, should be avoided, if a good balance is to remain so. See the installation at Breteuil (p. 39); the balances on isolated piers, manipulations by rods from a distance, and the pointer observed through telescopes.

6. THE WEIGHTS, if obtained from a good maker, will stand the tests to a small fraction of a milligramme. First compare the tens; then one of these with all units (5, 2, 2, 1). Next balance the two tens against the one twenty. Finally all these against the fifty. Like tests the fractional grammes are subjected to. For all work here considered, these tests should be fully met by the weights. For work of higher pre-

cision, the actual errors are determined in hundredths of the milligramme by the method of oscillation, not here considered.

7. All our WEIGHINGS are made IN AIR; but air buoys up all bodies to the extent of the weight of the air displaced by the body on the scale pans. This is ARCHIMEDES' principle, applied to air.

Now, a cubic centimeter of air, under common conditions, weighs one and one fifth milligrammes (1.2 mgr). For a fifty gramme specific gravity flask, this amounts to 60 milligrammes or 6 centigrammes. This is evidently too much to be overlooked. See 3, 12 and 38, Note.

8. Ordinary weights are made of turned brass, highly polished or finely gilt (2, 7). The specific gravity of brass is 8.4; consequently the weights balancing 50 cc water occupy about 6 cc, and therefore are buoyed up 7 mgr.

If we had actually 50 cc of water on the one pan, and 50 gramme weights on the other, there would be NO EQUILIBRIUM. The water would be buoyed up 60 mgrs., the weights by 7 mgr; that is, equilibrium would be obtained by 49.947 grammes, showing an error of 53 mgr. for 50 cc of water.

9. In all accurate work, this buoyancy of the air must be allowed for. This correction applied to the APPARENT WEIGHT on the balance, gives the ABSOLUTE WEIGHT, which the body would show, if weighed in vacuo. Hence this correction is also called reduction to vacuum. For every gramme, the correction amounts to the number of milligrammes K given in the following table, varying with the specific gravity G of the body weighed. These values are determined as above.

Add.		Add.		Subtract.	
G	K	G	K	G	K
0.8	1.36	3	.26	9	0.01
1.0	1.06	4	.16	10	.02
1.2	0.86	5	.10	12	.05
1.4	0.71	6	.06	14	.06
1.6	0.61	7	.03	16	.07
1.8	0.52	8	.01	18	.08
2.0	0.46	8.5	.00	20	.09

Thus 32.254 grammes of magnesium, G 1.75 give K 0.54 mgr. per gramme; the correction therefore is 17.4 mgr. and the absolute weight 32.271 grammes.

10. It is true that this correction will fluctuate slightly with the varying condition of the atmosphere as to temperature and pressure; but the latter CORRECTION OF THE CORRECTION is an entirely insignificant quantity and therefore commonly disregarded. Minute quantities of second order are always practically nothing.

11. If, for analysis, any suitable amount of the substance has been taken, it is carefully dried (in the exsiccator, over concentrated sulphuric acid) and then weighed ( $q$ ). Now the analytical operations are performed, the substance converted into some new compound, and this weighed ( $p$ ). Then the ANALYTICAL RATIO  $a = p/q$  has been determined; it is the weight of the determined substance PER UNIT of the given substance. A number of such determinations give a MEAN VALUE representing the average result of all determinations.

12. Finally, this ratio is compared to the ATOMIC RATIO  $r$  calculated from the chemical formulæ of the two substances (the one taken and the one formed) with the accepted atomic weights. If the analytical ratio agrees with the atomic ratio, the substance is proved pure, 100 per cent. strong. Inversely, if the substance had been prepared with utmost care, as pure as possible, its analytical ratio agreeing with the atomic ratio, demonstrates the correctness of the chemical formulæ and the atomic weights used.

---

NOTE. For any one series of analyses of the same given substance, determining the same substance formed therefrom, the analytical ratio must be constant; it may fluctuate slightly, according to the varying imperfections of method and work, but it should not show any signs of SYSTEMATIC VARIATION with the amount of substance taken. If it does, such variation indicates a source of gravest error.

This is the case with the famous determinations of Stas (see p. 79). Therefore, his conclusions are without foundation. 41, 12.

## 47. SPECIFIC GRAVITY METHODS.

1. The physical methods of analysis (45.6) are all very useful and interesting, but we have time for specific gravity determinations only (2, 11, 12). These methods are both practical and quite exact within their proper sphere. It will be easiest to first consider liquids; the methods may thereafter be readily applied to solids also.

2. THE GRADUATED CYLINDER weighed empty and again when filled to any mark, gives both weight and volume of the liquid; hence its  $G$ . Weighing to the decigramme, estimating the volume to the tenth cc, it requires 20 to 40 cc to obtain results worth calculating to two places. The importance of the method is its perfect clearness. It forms the simplest and best introduction to specific gravity work.

3. THE LITER FLASK has a spherical form with cylindrical, narrow neck, on which is the mark. The best flasks are provided with ground glass stopper; the bottom is flattened, the glass thin and the flask light.

Weigh empty and filled to mark (3, 5); as the flask has a definite capacity (10, 25, 50, 100 cc), all data are known. The first practice consists in verifying the capacity of the flask by using water, the temperature of which should be observed and recorded. Weigh to centigramme. Calculate three decimals.

4. THE PYKNOMETER or true specific gravity flask, is usually provided with a ground glass stopper having a capillary perforation. The filling must be done carefully. Flask only handled by points of two fingers, at the neck. Weigh to the milligramme; calculate  $G$  to four decimals. First use water to test the capacity of the flask, and find the variations due to changes in temperature. The Sprengel tubes are not required for this course.

5. In all these cases it is essential that THE VESSEL BE CLEAN AND DRY before filling, and dry on the outside before weighing. The latter is done by means of soft filter paper. Working an aqueous solution exclusively, washing with water, followed by careful filming (3, 3, Note) is sufficient. If changing to another class of liquids, wash, rinse with water, rinse with alcohol, film with ether and dry by a current of air from a foot blower.

6. The specific gravity of SOLIDS, in fragments, is determined by cylinder, flasks and pyknometer, using water if the solid is insoluble therein, otherwise some liquid (ether, benzole), in which the solid is insoluble. Always take a relatively large amount of solid, in comparison to the capacity of the vessel; this secures higher accuracy. Air bubbles must be removed; glass rod or platinum wire may be used for that purpose.

7. The solid having been weighed separately ( $w$ ), also the flask filled with liquid ( $a$ ) and containing the solid with liquid ( $b$ ), we have evidently the loss  $w + a - b$  as the weight of the liquid displaced by the solid. If the liquid be water, then this is the volume  $v$ , and the specific gravity results by the usual division. If not water, the gravity  $g$  of the liquid must be determined; divided into the loss, the quotient will be the volume  $v$  of the solid sought. Calculate as many decimals as before directed.

8. Any balance is readily converted into our form of HYDROSTATIC BALANCE by placing a crystallizing dish on the bench over the left hand scale pan, suspending by a thin platinum wire, a perforated platinum scale pan from the hook into the water, all adjusted in such a manner that when the beam is released, this submerged pan will be midway between surface of the water and the bottom of the dish. On such a balance, the body is weighed first in air ( $w$ ), then in water ( $a$ ); evidently,  $w - a$  is the volume  $v$ , so that  $G$  can be calculated. Number of decimals depends on the character of the balance.

9. No correction need be applied on account of the expansion of the glass vessels used; for this amounts to only one forty-thousandth per degree. But the EXPANSION  $e$  OF THE WATER per unit is notable, as given below in thousandths (or units of third decimal). Since the standard is water at its greatest density (4 degrees), the correction is the product  $eG$  in the third place, which must be subtracted from  $G$  to obtain the corrected  $G'$  referring to water at 4 degrees.

10. Expansion  $e$  of one cubic centimeter of water in units of third place (thousandths):

t	e	t	e	t	e	t	e
0	0.13	16	1.03	30	4.3	70	22.7
4	0.00	20	1.77	40	7.7	80	29.0
8	0.12	24	2.68	50	12.0	90	35.8
12	0.47	28	3.79	60	17.0	100	43.2

Reduction to vacuum may be necessary also. Suppose the division of volume into weight had given  $G$  10.147 for silver at 20 degrees; then  $e$  1.77 times  $G$  gives 18 in third place, hence  $G$  reduced to 4 degrees is 10.129.

11. These methods are applied to the determination of the strength of salt solutions, commercial and pure acids and alkalies, sugars, which are heavier than water, also alcohol and ammonia which are lighter. The specific gravity found, generally reduced to water at 4 degrees, is looked up in the tables of handbooks and the percentage of strength corresponding hereto is taken from the tables. A simple INTERPOLATION may be necessary to give the exact value if the value of  $G$  is not in the table. Heavy metal solutions should also be used, such as  $Ka\ lo-Hgate$ .

12. Work on solids is suitably connected with the study of important crystals, salts, metals, minerals and ores. Ordinary specimens may be used in cylinder and flasks, the finest, such as gems, cleavage pieces, rarer metals, are excellent for determination by the hydrostatic balance. Carried on in this manner, specific gravity work becomes as interesting as it is practically useful.



TABLE. This short table gives the number of milligrammes which a cubic centimeter of the following 10 per cent. solutions weighs in EXCESS of one gramme:

	Hate	Clide	Nate	Sate	Cate
H	0	49	58	68	—
Ka	92	65	64	(83)	92
Na	111	72	67	92	105
Clide:	Am 30,	Ca 86,	Ba 94.	—Ag	Nate 90
Sate:	Mg 105,	Cu 103,	Zn 108.	—Pb	Acet. 76

For about 5 per cent. either way, changes in G are proportional to amount dissolved, and can be calculated readily. Sucrose 40.

Lighter than water (mgr. less than 1 gr.) are for 10 per cent. solutions: Ammonia 42, alcohol 14.

## 48. ANALYSIS BY DISSOCIATION.

1. Analysis by means of the physical agencies (45.7) and without the use of reagents proper or change of vessel, is necessarily capable of a HIGH DEGREE OF PRECISION. Thus Richards, obtained in three series of electrolyses, 0.25455, 0.25450 and 0.25448 of metallic copper per unit of blue vitriol; the mean is 0.25451. Precisely the same value results by calculation from the formula  $\text{Cu O}_4\text{S} + 5 \text{H}_2\text{O}$  for Cu 63.5, confirming this value.

2. Electrolysis having been considered sufficiently (35, 36, 37), we may devote this lesson mainly to DISSOCIATION, that is, chemical decomposition by means of heat. If violent and complex actions are avoided, this method of quantitative analysis can furnish very accurate results, there being absolutely no reagents used (not even solvents as in electrolysis in the wet way) and no change of vessels is necessary during the process.

3. Another important excellency of this method we have in the fact that the portion of matter, driven off by heat, can

generally be collected for qualitative examination or for weighing. Thus the dissociation may be CHECKED, both as to kind and amount of the volatile substance driven off.

4. It is, however, necessary that the DEGREE OF HEAT employed be reasonably constant and well selected. The water bath, sand bath and air bath are sufficient to drive off the more volatile constituents, such as water and many acids. A dull red heat, just making the crucible glow, or a bright red heat, may be maintained by a Bunsen Burner, properly regulated. A real white heat requires the use of blast or furnace.

5. THE SUBSTANCE to be analyzed must be pure, entirely free from volatile impurities, such as humidity or hygroscopic water. Pulverization and drying over concentrated sulphuric acid in the exsiccator, or in a current of dry air, are commonly resorted to. Some crystallized bodies lose WATER of crystallization by this means, unless the temperature is kept low. Examination by the microscope will show efflorescence, if water is lost in this way.

6. Determinations of the WATER OF CRYSTALLIZATION are especially interesting and instructive. The sand or air bath will answer; temperature about 200 degrees. Gypsum, blue vitriol, alum, borax, are a few of the more common cases. The formulæ are  $\text{Ca O}_4\text{S} + 2 \text{H}_2\text{O}$ ;  $\text{Cu O}_4\text{S} + 5 \text{H}_2\text{O}$ ;  $\text{K}_2\text{O}_4\text{S} + \text{Al}_2 (\text{O}_4\text{S})_3 + 24 \text{H}_2\text{O}$ ;  $\text{Na}_2 \text{O}_7 \text{Bo}_4 + 10 \text{H}_2\text{O}$ ; they permit the calculation of the amount of water per unit of weight (atomic ratio, 46, 12) which will check the amount actually obtained by the determination (the analytical ratio, 46, 11).

7. AT A RED HEAT, in a platinum or porcelain crucible over a Bunsen flame, many important analyses by dissociation are made. Blue vitriol leaves copper oxide,  $\text{Cu O}$ . Lead nitrate  $\text{Pb} (\text{O}_3\text{N})_2$  leaves lead oxide  $\text{Pb O}$  (in porcelain crucible). Potassium bicarbonate,  $\text{Ka H O}_3\text{C}$  leaves the carbonate  $\text{Ka}_2 \text{O}_3\text{C}$ ; of course, two atoms of the former yield one of the latter. Potassium bitartrate  $\text{Ka H C}_4\text{H}_4\text{O}_6$  yields the

carbonate also. Crystallized Am-Mg phosphate  $\overset{\text{Am}}{\text{Mg}}\text{O}_4\text{P} + 6\text{H}_2\text{O}$  yields Mg pyrophosphate,  $\text{Mg}_2\text{O}_7\text{P}_2$  in all gravimetric phosphate determinations.

8. Dissociations requiring a WHITE HEAT necessitate the use of the blast flame under the platinum crucible. The fire-clay (Erdmann) or graphite cylinder around the crucible, facilitates the work. Examples are common, results quite accurate. Calcite and any calcium carbonate  $\text{CaO}_3\text{C}$  yields the oxide, lime,  $\text{CaO}$ . Magnesium carbonate yields the oxide already at a red heat.

9. In all cases, the determination involves the weighing of the vessel, taking substance and weighing the vessel with the substance; igniting, chilling on iron, cooling in exsiccator, weighing; repeating this process TILL CONSTANT WEIGHT OBTAINED, that is, no further loss sustained by renewed ignition. In all cases, the analytical ratio obtained should be compared with the atomic ratio calculated from the formula.

10. The most useful technical analysis of coal is a process of dissociation, carefully worked out by the author in 1867 and 1868 (American Journal of Mining, New York, also in German and English periodicals) have become part of general chemical practice. The remarkable increase in weight when bituminous coals are dried for the determination of moisture, was discovered in this research, and is due to oxidation of the bitumen at low temperatures.

---

NOTES. The student should, for practice, calculate the atomic ratios for the cases specified, and compare the results with the following:

6. Gypsum 0.7907. Blue Vitriol 0.6393. Ka-Alum 0.5443.

7. Blue Vitriol 0.3186. Lead Nitrate 0.6254. Ka Bicarbonate 0.6900. Ka Bitartrate 0.3670. Am Mg Phosphate 0.4531.

8. Ca Carbonate 0.5600. Mg Carbonate 0.4762.

## 49. GASOMETRIC ANALYSIS.

1. Gasometric Analysis has been DEFINED (45, 9) and characterized (45, 5); we have also quite extensively practiced it (18, 8-11; 24, 7) and learned to distinguish it from GAS-ANALYSIS (32; 33, 3-11; 45, 9). We shall now briefly state OUR SPECIAL METHODS of reduction and work in this fascinating and admirably simple process of analysis.

2. The law of Avogadro (40, 10) asserts that the molecular volume of all gases, at the same temperature and pressure, is the same. For practical work, the milligramme is our unit of weight; the mgr. molecule of hydrogen gas our unit of volume. We disregard temperature and pressure by CHEMICALLY DETERMINING THIS UNIT OF VOLUME EXPERIMENTALLY, i. e. the volume occupied by the hydrogen produced from 24 mgr. magnesium.

3. This MGR.MOL.VL. is always nearly 24 cc at ordinary pressures and temperatures, at which gasometric work is done in the laboratory. That is, having dissolved an accurately (to tenth mgr.) weighed amount of pure magnesium, and measured the gas volume produced in cc, the quotient of the volume, divided by the weight, differs by but a small fraction from unity; say by  $e$  per cent. Then all volumes observed in analysis, at the time, must be reduced that number of per cent., to bring the volume to our standard.

4. Our ordinary GAS BURETTE is the simplest possible, readily made from any Mohr's burette and a pipette, as shown in our plate of Apparatus. We also make use of the Hempel gas burette with perforated stop cock, (3, 10, 11) but in reversed position, and provided with pipette-reservoir; we use this both with water and mercury. A simple water-jacket, consisting of a glass tube surrounding the burette and exceeding it about 6 mm in width, filled with water, suffices. A thermometer is inserted in the pipette-bulb receiver.

5. OUR EVOLUTION VESSELS vary considerably, according to the object for which they are used. The simplest is an ordinary test tube, fastened by means of a cork in a cylindrical stand glass but little wider, the space being filled with water, while the test tube, by means of perforated stopper, allows connection with the burette by rubber tube of small bore.

We work the evolution at all temperatures, the only condition being that the temperature is the same at the final and at the initial reading of the burette.

6. When necessary we insert between the evolution vessel and the burette our AIR LOCK, simply a U-tube of proper capacity (100 or 200 cc) having enough lead foil wrapped around one branch to stay down in a tall beaker with water; by judicious use of black paint, the lead sticks to the glass and does not corrode. At the close of each determination, after detaching the evolution vessel, a few motions of the reservoir thoroughly ventilate the air lock, filling it with atmospheric air. The principle here used is that of displacement.

7. Gases acting upon air are handled IN ANY SUITABLE GAS; thus nitric oxide in hydrogen. In such experiments the Hempel burette is most serviceable, on account of that perforated stop cock. A Kipp and the necessary washing flasks are connected with the evolution vessel, by means of a tube with stop cock.

The determinations being very rapid, hydrogen does not leak appreciably; but using an air lock connected by glass tubing, even this error may be overcome entirely.

8. Under these conditions, the reduced gas (3 and 4 above) weighs per cubic centimeter as many milligrammes as its molecular weight divided by 24. That is, a cubic centimeter of the following gases, after such reduction, weighs the number of milligrammes stated: H, 0.083 ( $\frac{1}{12}$ ); N, 1.166 ( $1\frac{1}{6}$ ); O, 1.333 ( $1\frac{1}{3}$ ); Cl, 2.958 ( $2\frac{23}{4}$ ); NO, 1.250 ( $1\frac{1}{4}$ ); CO<sub>2</sub>, 1.833 ( $1\frac{5}{6}$ ). Urea C H<sub>4</sub> O N<sub>2</sub>, 2.500 ( $2\frac{1}{2}$ ). Sweet spirits of nitre, 3.125 ( $3\frac{1}{8}$ ).

For solubility allow a volume equal to that of the liquid used in the case of NO and CO<sub>2</sub>.

9. As to PROCESSES employed, hydrogen is produced by acids and magnesium; carbon dioxide by acids and most carbonates; nitrogen from urea and a strong, fresh solution of hypobromite; chlorine from hypochlorites or chlorine water and peroxide of hydrogen; oxygen from permanganate and peroxide of hydrogen; nitric oxide from sweet spirits of nitre, Ka loide and H Sate in an atmosphere of hydrogen. The substance used as reagent must be in excess; in the last example, there must be an excess of permanganate if the peroxide is to be determined, while if permanganate is to be determined, an excess of peroxide must be taken.

10. The QUANTITATIVE RELATION between the VOLUME of the gas produced and the WEIGHT of the substance taken must be carefully established before the process can be accepted. The reaction must also be quick and complete.

For hydrogen, we obtain one equivalent for each equivalent of metal dissolved. But this process, being fundamental, we use to determine the unit or equivalent volume of hydrogen itself, to make us independent of variations in temperature and pressure.

11. Carbonates give one molecule of fixed air for each double equivalent. Consequently, 100 mgr. Ka Bicarbonate must yield 24 cc gas; or every cc gas represents 4.16 mgr. of the true bicarbonate. Thus the percentage of pure bicarbonate in the sample taken becomes known. In the same way, each cc nitrogen gas representing 2.5 mgr. of urea, the gas evolved from a measured quantity of urine gives its per cent. of urea. Hypochlorites give a volume of oxygen gas exactly equal to that of the effective chlorine; or 2 Ca OCl=183 yield one molecule O, hence every cc gas corresponds to 7.625 Ca hypochlorite.

12. It will readily be seen that this method of analysis has received a considerable extension at our hands. Further details will be given in the laboratory course.

As to CALCULATIONS, one example will suffice. Suppose 42.7 mgr. Mg gave 44.5 cc gas; hence 1 mgr. gave 1.042 cc; reduction 4.2 per cent.

Peroxide of hydrogen, mixed with an equal volume of dilute sulphuric acid; 5 cc mixture gave, with excess of permanganate, 57.2 cc gas. The 4.2 per cent. is 2.4 cc, leaving 54.8 cc reduced; hence 10.96 vols.; weight one and a third gives 14.61 mgr. oxygen per cc peroxide, or 1.46 per cent. by weight of oxygen; or 3.1 per cent. peroxide, by weight.

---

NOTE. A cubic centimeter of dry air weighs 1.2 mgr. at the following temperatures and pressure (mm):

t	1	5	9	13	17	21	25	29
p	710	720	730	740	750	760	770	780

The CHANGE in weight amounts to ONE PER CENT. for 3 degrees in temperature and for 7 millimeters pressure.

By this simple table of reduction, the weight may be calculated from the observed pressure and temperature. For example, at 18 degrees and 735 mm, we calculate from nearest 17 degrees 750, as follows: 1 degree high, weight  $\frac{1}{3}$  per cent. low; 15 mm low, weight 2 per cent. low; total  $2\frac{1}{3}$  per cent. low, on 1.2 mgr. is 0.028 low, say 0.03: hence weight of one cc air at 18 degrees and 735 mm is 1.17 mgr.

Same correction per cent. must be applied to weights given in 8 if this mode of reduction by barometer and thermometer reading be preferred.

In this mode of reduction, it must be remembered that the vapor pressure must be subtracted from the reduced barometer reading to get the pressure of the dry gas required. This vapor pressure is, in mm mercury:

temp.	6	10	14	18	22	26	30
vap. press.	7.0	9.1	11.9	15.4	19.7	25.0	31.6

For chemical purposes, the reduction given in the text is both easiest applied and most rational.

## 50. VOLUMETRIC ANALYSIS.

1. This excellent method of quantitative analysis has been exemplified in lecture 24 for the measurement of acids and bases. A general definition thereof has also been given (45.10). This method of analysis was founded by GAY-

LUSSAC (1824 to 1832) and was brought into system by MOHR (Titrimetric-Method, 1855). We will now present the leading principles and modes of practice of the same.

2. The two kinds of TEST SOLUTIONS introduced by these chemists continue in use—each being most convenient in its own sphere. When many determinations of the same kind have to be made, the Gay-Lussac STANDARD SOLUTION, representing a centigramme or milligramme of the substance per cubic centimeter, is used. If a greater variety of work has to be done by the least number of test solutions, the NORMAL SOLUTIONS of Mohr are the most practical.

3. Silver,  $\text{Ag}=108$  is precipitated by salt,  $\text{Na Cl}=58.5$ ; accordingly the atomic ratio of silver to salt is  $1 : 0.5417$ . A cubic centimeter of salt solution will therefore precipitate one milligramme of silver, if it contains 0.5417 mgr. salt per cc, or 0.5417 grammes per liter. A cubic centimeter of salt-solution will precipitate a centigramme of silver, if it contains 5.417 grammes of salt per liter. Such solutions are standard solutions according to GAY-LUSSAC; the number of cubic centimeters used directly gives the weight of the silver or substance sought.

4. The normal solutions of MOHR contain a milligramme-equivalent per cubic centimeter (24.6 and 45.10). A normal salt solution therefore is made by dissolving 58.5 grammes of pure sodium chloride to a liter; and each cubic centimeter thereof will precipitate one milligramme-equivalent of silver, that is 108 mgrs. A tenth-normal salt solution is made dissolving 5.85 gr. salt to a liter, and each cc thereof precipitates 10.8 mgr. silver.

5. The Mohr solutions can also be used to determine the PER CENT. STRENGTH of any given substance, without calculation, by WEIGHING OFF A PROPER QUANTITY, determined by the equivalent weights. Thus if each cc of the tenth normal solution is to represent one per cent., the total 100 per cent. silver must equal 100 cc tenth normal or 10



normal = 10 times 108 mgr. = 1.080 grammes of silver. If this amount of silver (alloy) is dissolved, it will require as many cc tenth normal salt solution as it contains per cent. of pure silver. In general, take 100 mgr. equiv. and 1 per cent. will be precipitated by 1 cc N solution.

6. We have now presented really all principles required in the calculation of volumetric work. Suppose the strength of aqua ammonia were to be determined by normal acid in per cent. of ammonia gas,  $\text{NH}_3 = 17$ . Then 100 cc normal would contain 1700 mgr.  $\text{NH}_3 = 1.7$  gramme. Take 1.7 grammes of the aqua ammonia, and neutralize with normal acid; the number of cc used evidently are the per cent.  $\text{NH}_3$  gas in the liquid. If half the quantity be taken, every cc normal acid represents 2 per cent.

7. Of the principal lines of volumetric work, NEUTRALIZATION has already been considered (Lect. 24). In practice, each cc of normal acid measures an equivalent amount of alkali; that is, one mgr. equiv. In numbers, 17 mgr. ammonia; 40 mgr. Na Hate ( $\text{Na OH}$ ); 56 mgr. Ka Hate ( $\text{Ka OH}$ ). In the same way, each cc normal alkali measures one mgr. equiv. of any acid. In numbers, 63 mgr. nitric ( $\text{HO}_3\text{N}$ ); 49 mgr. sulphuric  $\frac{1}{2}(\text{H}_2\text{O}_4\text{S})$ .

8. THE CHAMELEON PROCESS has been considered so far as to show that every 2 atoms of the reagent ( $\text{Ka O}_4 \text{Mn}$ , = 158) set free 5 atoms of oxygen (10 equivalents); or 1 mgr. equivalent oxygen corresponds to 31.6 mgr. of pure permanganate. Tenth-normal requires 3.16 gr. per liter.

The standardizing is done with the pure, crystallized hydrated ammonio-ferrous sulphate,  $\text{Am}_2\text{O}_4 \text{S} + \text{FeO}_4\text{S} + 6 \text{H}_2\text{O} = 392$  (see 15, 11). Two of this salt require one atom of oxygen (see 44.9) hence 39.2 is tenth-normal. In the presence of a large excess of sulphuric acid, the reaction is quick and sharp. Add permanganate to acid ferrous solution till color no longer disappears. The so-called "florist's wire" generally used for standardizing, is not pure iron.

9. THE IODINE PROCESS, due to Bunsen (p. 24) is typified in the reaction between the HYPO and the iodine solution; using a trifle of starch paste as indicated (BLUE with smallest trace of FREE iodine, 23, 4). Pure, crystallized Na Hyposulphite is represented by  $\text{Na}_2\text{O}_3\text{S}_2 + 5 \text{H}_2\text{O} = 248$ . Two of this THIOSULPHATE react with two iodine, giving two Na Io and the so-called tetrathionate  $\text{Na}_2\text{O}_6\text{S}_4$ ; hence 248 hypo correspond to 127 iodine. Tenth-normal hypo must contain 24.8 mgr. per cc, and is equivalent to 12.7 iodine, or 8.0 bromine, or 3.55 chlorine. The iodine is kept in solution by an excess of Ka Ioide—best twice the weight of the iodine. Twentieth normal is more convenient for use.

10. PRECIPITATION of neutral chloride by silver permits the use of Ka Crate as indicator; when all Clide precipitated as Ag Clide, the next drop will show the red color due to Ag Crate (Mohr).

A tenth-normal Ag Nate solution is obtained by dissolving 17 grammes of the nitrate ( $\text{Ag O}_3\text{N} = 170$ ) to the liter. Every cc hereof will represent the following equivalents: 5.85 mgr. Na Cl; 15.0 mgr. Na Io; 7.45 mgr. Ka Cl; 16.6 mgr. Ka Io; 8.7 mgr. Li Br; 15.5 mgr. Fe Io<sub>2</sub>. These data are easily calculated from the formulæ given.

## 51. GRAVIMETRIC ANALYSIS.

1. In gravimetric analysis, a weighed amount of the substance is chemically changed to some well-defined compound, sufficiently permanent to permit accurate weighing. The chemical formula of this compound will tell how much it contains of the ingredient to be determined. Thus the amount in a UNIT OF WEIGHT of the original substance becomes known. See 45, 11.

2. Suppose that the amount of CALCIUM in a given substance were to be determined. The weighed substance is dissolved in acid, filtered; heavy metals removed, if

present; filtrate made ammonical and the calcium precipitated as oxalate, that being the most insoluble calcium compound. Filter, wash, dry on water bath, weigh the crystallized oxalate,  $\text{Ca O}_4\text{C}_2 + \text{H}_2\text{O} = 146$ . In platinum crucible, at dull redness, it changes to carbonate,  $\text{Ca O}_3\text{C} = 100$ , which weigh. Ignite with blast at white heat; it becomes the oxide (or lime)  $\text{Ca O} = 56$ , which weigh.

3. From the formulæ given it is easy to CALCULATE that a unit of weight of crystallized oxalate represents 0.2740 of Ca, the carbonate 0.4000 and the oxide 0.7143 of Ca. In a like manner the oxalate represents 0.3836 of oxide and the carbonate 0.5600 thereof. If then, any of these compounds found had been weighed, the corresponding amounts of Ca or of Ca O is readily calculated by the values just given. In this way the percentage in the original substance becomes known.

4. Now, which of these compounds gives the MOST ACCURATE RESULTS? Not the oxalate, for it is difficult to avoid a loss of water of crystallization in drying the precipitate; not the carbonate, for overheating reduces it to oxide, insufficient ignition may leave some oxalate. Evidently, the oxide, obtained last is the best compound to use, for it need only be ignited till constant weight, since it is not volatile at all.

5. We have already shown that SILVER is weighed as CHLORIDE (45, 11). It need hardly be added, that chlorides are determined in the same way, by the same compound, upon adding an excess of silver solution.

The calculations are based upon the formula  $\text{Ag Cl} = 143.5$ . Every 143.5 Ag Cl<sup>ide</sup> weighed represent 108 silver in the original; or the weight of Ag Cl<sup>ide</sup> found, multiplied by 0.7525, will give the weight of the silver.

6. In the same manner the exceedingly insoluble Ba Sate is formed and weighed for the determination of the amount of sulphate—by adding Ba solution; and for the determination of barium—by adding a soluble sulphate. To obtain accurate

results, the MINUTIÆ of the operation must be studied and practiced; precipitation, washing, igniting, in fact, every operation has to be as nearly perfect as possible in order to obtain reliable results.

7. Another compound of great importance in gravimetric analysis, is the crystallized hydrated ammonio-magnesium phosphate, almost absolutely insoluble in ammoniacal (Clide and Hate) solutions. After filtering and washing it is dried, ignited and weighed as magnesium pyrophosphate (48.7). The  $\text{Mg}_2 \text{O}_7 \text{P}_2=222$  represents  $\text{P}_2 \text{O}_5=141$  of the so-called anhydrous phosphoric acid and 80 of Mg O. That is, 0.6351 thereof is  $\text{P}_2 \text{O}_5$  and 0.3603 is magnesia, either of which is so determined.

8. The metals may often be determined as oxide. Thus iron compounds are generally determined as ferric oxide  $\text{Fe}_2 \text{O}_3=160$ . Ferric salts are directly precipitated by ammonia, filtered, washed, ignited and weighed; ferrous are readily oxidized with nitric acid to ferric, and treated as just stated. Since  $\text{Fe O}=72$ , 160 ferric oxide correspond to 144 ferrous oxide and to 112 iron. By these numbers the reductions necessary can be made.

9. Platinum chloride gives a crystallized precipitate of  $\text{Am Cl}_6 \text{Pt}$  with sal-ammoniac, especially when alcohol present. This salt,  $\text{Am}_2 \text{Cl}_6 \text{Pt}=443$  represents 36 ammonium and 194 platinum; ignited, it leaves only the latter, which thus represents 36 ammonium or 34 ammonia gas. This is only 0.0767 of the crystallized salt, thus may serve for accurate determinations.

10. The subject of quantitative analysis is as difficult as it is important. While only laboratory work will make these processes thoroughly understood and familiar, it is hoped that these carefully selected examples will suffice to make the student comprehend the methods employed and the value of the results obtained. While an application of chemical formulæ, quantitative analysis really is equally demonstrating the truth of the chemical formulæ themselves.

## 52. SPECTRUM ANALYSIS.

1. The rainbow shows a SPECTRUM of sun light. Looking through a prism at any narrow band of white, we see a corresponding series of colors. The least deflected from the straight line of sight, is the red; then comes orange, yellow, green, blue, indigo and violet, which is the most deflected. Newton (1671) first thoroughly studied the solar spectrum obtained through glass prisms.

2. In these spectra the colors blend and overlap. Narrowing the band of light—by means of an adjustable slit in the shutter of a darkened room—the colors become more distinct and pure, but at the same time, the total intensity becomes less. By observing through a telescope, more light enters the eye, the pupil of which is thereby virtually enlarged to the size of the object glass of the telescope. This was first done by Fraunhofer of Munich (1814). He obtained the best defined spectrum of the sun, the purest and most brilliant. But he was surprised to find many parts of the spectrum missing—replaced by fine black lines, the so-called FRAUNHOFER LINES of the spectrum. He counted thousands. The most notable he designated by the letters of the alphabet from A to H; groups of lines he marked a, b. See upper spectrum, p. 72.

3. For greater convenience, Kirchhoff (p. 35) and Bunsen (p. 24) combined all these pieces of apparatus on one frame, and called the instrument resulting, a SPECTROSCOPE (1860). For ordinary chemical work, the DIRECT VISION spectroscope is the most convenient. It has the narrow, adjustable SLIT turned towards the light. Then comes a powerful SYSTEM OF PRISMS (of 3 crown and 2 flint glass prisms); finally a small telescope. All these parts are enclosed in one tube.

4. Looking through such a spectroscope at the sky, first narrow the slit till almost shut, then slide the telescope in or out till distinct vision of the Fraunhofer lines. The black line

D in the yellow, and the line E in the green near the group b will be readily recognized. The instrument is now ADJUSTED for chemical work.—It is best to revolve the spectroscope till the spectrum appears horizontal with the red to the left, as they are conventionally represented in spectrum plates (p. 72).

5. Looking at the colorless flame of a Bunsen Burner, it will be almost invisible; a yellow line may flash up from time to time, due to traces of sodium almost everywhere. Introducing a clean (ignited till imparting no color to flame) platinum loop that has touched a sodium compound or solution, a brilliantly luminous line will flash up in the yellow. If the Bunsen flame is so placed that good daylight can enter the spectroscope through the flame, the solar and the sodium spectrum will be seen simultaneously. The yellow sodium line is then seen to coincide with the line D. There is sodium in the sun.

6. The spectra of the elements which can be observed in this manner, using the heat of the Bunsen flame only, are mapped on page 72. The most characteristic bright lines are: extreme red for Ka; brilliant red (near C) Li; blue line (beyond F), Sr; brilliant orange, yellow and green line, Ca; group of 3 or 4 bright green lines, Ba. By the two lines in the violet, Bunsen recognized the NEW ELEMENT rubidium (Rb). By the two lines in the blue, he found caesium (Cs). The extremely bright, but very transitory line in the green, revealed Thallium (Tl) to Crooks of England and Lamy of France.

7. By means of the electric sparks of a Ruhmkorff coil, the heavy metals are volatilized in minimal quantities, but sufficient to show their spectra brilliantly. These spectra are too complex, consist of too many lines, to be useful in ordinary chemical practice.

The discharge of the coil through rarified gases (in Pluecker tubes, contracted in the middle) gives fine line spectra for ready chemical identification. The hydrogen spectrum consists of a red and a blue line, coinciding with the Fraun-

hofer C, F and a violet line near G. By its spectrum, argon is distinguished from nitrogen (38, 10).

8. At lectures, before the general public, many of these phenomena are projected on the screen. For scientific students it is preferable to show these phenomena individually at an EXHIBITION, where the different instruments are in charge of one or two students each, who, by their advanced work in the laboratory, have become familiar therewith. This is the only way to show the flame and gas spectra in their real beauty.

9. Twenty years ago, a line in the spectrum of the solar corona was discovered, on the absolute or wave length scale at  $D_3=587.5$ , near the Na line, which shows double in such powerful instruments, at  $D_2=588.9$ , and  $D_1=589.5$ . No terrestrial element showing that line, it was ascribed to some hypothetic element peculiar to the solar corona, and named Helium.

10. When Lord Rayleigh had discovered argon in the air, Professor Ramsey, searching for mineral sources of argon, found a gas, giving the characteristic  $D_3$  line, on treating Cleveit with sulphuric acid (1895). This gas is that substance of the solar corona called Helium. Its density is twice that of hydrogen, its atomic weight is taken at 4. Like argon, it is nullovalent, does not combine chemically. One gramme of cleveit (a rare Uranium mineral) gives about 7 cc helium gas. It has also been found in rare Yttrium minerals (Fergusonite, Samarskite).

11. If a direct vision spectroscope be substituted for the eye piece of a telescope, the spectra of the stars and nebulae can be observed, as well as the spectrum of any part of the sun, its spots, protuberances and other details. Huggins, Janssen, Lockyer and others have developed this part of astronomy which may be considered as COSMICAL CHEMISTRY. Father SECCHI (p. 29) has labored most successfully in this field, and first classified the stars according to their

spectra, i. e. their chemical composition. The telescope of Galilei showed the form (p. 44) while the spectroscope reveals the chemical nature of the stars.

12. When the spectroscope is directly against the bright sky so as to show the solar spectrum well, a test tube, containing a dilute solution of any coloring material, held before the slit, will blot out parts of the spectrum, sometimes showing definite black lines. These spectra are called ABSORPTION SPECTRA. The spectra of chlorophyll, red blood (arterial) and blue blood (venous) are quite characteristic. These absorption spectra are most useful to organic chemistry.

### 53. DRY WAY ANALYSIS.

1. After having shown how the chemical formulæ of compounds are established and applied for quantitative determinations, we will complete the introduction to the inorganic part of chemistry by a systematic exposition of the principal QUALITATIVE TESTS, both in the dry and the wet way. This course we have found much more interesting and useful than a synopsis of systematic chemistry.

2. The chemical blowpipe has been described (Lect. 5) and its use has been frequently required (Lectures 5, 6, 7, 9, 10, 11, 18, 26). We have learned to appreciate the blowpipe reactions (PYROGNOSTICS) because they require but a small instrument and a few of the simplest reagents, while giving definite results quickly and with but little labor—provided some skill has been acquired. All the typical tests can be well shown at lectures, so that even those who do not practice themselves will quite well understand the subject.

3. THE FIRST TEST is made by heating a minute sample on charcoal. The general results to be looked for are: 1, complete VOLATILIZATION, with or without odor; 2, a RESIDUE (i. e. where the substance was placed), and noting whether this residue is WHITE or NOT WHITE, also whether it pro-



duces FLAME COLORATION. Next look for an INCRUSTATION, i. e. deposit forming at some distance from the sample; and lastly, look for a REGULUS. Compare diagram, p. 73 (dry way).

4. If the substance volatilizes completely, repeat the experiment and examine carefully whether an ODOR can be recognized; that of burning sulphur proves S; of garlic, some As compound. If no odor, heat the substance with lime in a blowpipe glass tube; a distillate of white, metallic globules proves an Hg compound; odor of ammonia, an ammonium compound.

5. If the RESIDUE IS WHITE, it may show a) FLAME COLORATION or simply be an incandescent b) INFUSIBLE mass. In the first place (a) repeat the test on the platinum loop: flame yellow, Na; yellowish-green, Ba; orange, Ca; crimson, Sr; violet-purplish, Ka. Of these flames, Na, Ba, Ca are invisible through blue glass, through which Ka, Sr show finely; while these are invisible through a green glass which shows Na, Ba, Ca well. In (b) ignite after adding a drop of Co solution; color pale rose, Mg; green, Zn; blue, Al (see 7, 9).

6. If an INCRUSTATION has formed, note its color, size, and see whether there is also a regulus. Incrustation WHITE; very large, odor of garlic, As; smaller, nearer sample, with brittle regulus, smoking, Sb; white when cold, yellow while hot, Zn (try Co solution); YELLOW with brittle regulus, Bi, with malleable soft regulus, Pb; YELLOWISH, close to sample, regulus difficult except with cyanide flux, Sn; BROWN, no regulus, Cd; pale red, very light in amount, with fine white globular regulus, Ag.

7. A REGULUS WITHOUT INCRUSTATION may appear as GLOBULE (Cu, Ag, Au, see 7, 1-3) or as SPANGLES. In the latter case, the metal is generally not visible, except after cutting out the charcoal, grinding it under water in an agate mortar, and washing the light carbon particles off; the heavy, metallic, now partly flattened grains and spangles, will remain

at the bottom of the mortar. Pt, Ir, Pd are white, hard, very heavy, insoluble in acids; Fe, Ni, Co, are gray and magnetic. See 7, 11.

8. If no incrustation, no regulus, no white residue, but only a DARK COLORED residue remains, touch it with a good BORAX BEAD and fuse again. If the bead is BLUE, hot or cold, outer or inner flame, Co; if DEEP GREEN under all conditions, Cr; if hot green, cooling turns blue, Cu; BROWN, Ni; AMETHYST in outer, colorless in inner flame, Mn; YELLOWISH to ORANGE in outer, colorless or very pale green in inner flame, Fe. Compare 7, 11.

9. MICROCOSMIC SALT,  $\text{NaAmH O}_4\text{P} + 4 \text{H}_2\text{O}$ , when heated in the platinum loop, becomes metaphosphate  $\text{Na O}_3\text{P}$  which, like borax, dissolves metallic oxides and gives colored beads. We use these beads exclusively to recognize silicates and the chloroid compounds. The first leave an insoluble SKELETON OF SILICA (10.5; 11, 4) floating in the melted bead. To test for the latter, first saturate the bead with copper oxide, then add a trifle of the substance to be tested; flame colorations: blue,  $\text{Clide}$ ; blueish green,  $\text{Bride}$ ; intense green,  $\text{Ioxide}$ . Bead heated in glass tube, making inside dim (after washing),  $\text{Flide}$ .

10. SULPHATES, when mixed with pure soda and fused on platinum loop in inner flame, are reduced to sulphides; the fused mass placed on a silver coin, with a drop of water, blackens the silver, at least if a trace of muriatic acid is added (HEPAR REACTION). SULPHIDES give the odor of burning sulphur (9.3). NITRATES and CHLORATES deflagrate on charcoal, the latter especially violently. CARBONATES are best recognized by effervescence with an acid. BORATES tinge the flame green on its outer edges, especially on adding a drop of  $\text{HFl-Siate}$ . These are the principal pyrognostic reactions. Oxides give no reactions as negatives; they are recognized by their physical properties after other negatives are proved absent.

## 54. WET WAY ANALYSIS OF BASES.

1. In lecture 22 the metals were separated into 8 analytical groups, mainly by the use of hydrogen sulphide gas, and each metal was individually recognized by the specific peculiarities of the group reaction. We need only to add the most important DISTINCTIVE TESTS and a few specially delicate tests whereby TRACES of the metals may be detected. Methods of SEPARATION will also be indicated. We take up the metals by analytical groups.

2. THE GOLD GROUP is precipitated by  $H_2S$  in acid solution, the precipitate is soluble in yellow ammonium sulphide; the original solution is yellow to brownish.

GOLD is precipitated as metallic powder by a ferrous solution (best the ferrous salt, 15, 11); the precipitate appears brown in reflected, bluish in transmitted light; the dried precipitate shows metallic luster when pressed with a knife blade. Platinum is not precipitated by this reagent, except upon boiling.

PLATINUM solutions, when not too dilute, and containing  $HCl$ , yield a yellow precipitate with  $AmCl_3$ , forming splendid transparent yellow octahedral crystals, which can be studied under the magnifier or the microscope. Ignition leaves Pt sponge. 51.9.

3. THE ARSENIC GROUP is distinguished from the gold group by its solutions being colorless. The dry way reactions are especially valuable (53, 4, 6). The most sensitive test for ANTIMONY is given 37, 5; its solutions are also noted for giving a white turbidity with water, which promptly dissolves upon the addition of tartaric acid. Stannous solutions are precipitated white by mercuric chloride; stannic solutions not. Stannous solutions, containing a little stannic, (on addition of  $Cl$ -water) give purple of Cassius with gold solutions. Further special tests for As belong to toxicology.

4. THE COPPER GROUP is precipitated by hydrogen sulphide in acid solutions, and the precipitate is insoluble in yellow ammonium sulphide. Only Cu Side is slightly soluble in this solvent.

Am Hate precipitates all; the white precipitates of Hg<sup>ic</sup> and Bi are insoluble in excess; the blue precipitate of copper dissolves to sky blue solution, the white precipitate of cadmium dissolves to colorless solution with excess.

The hydrates precipitated by Ka Hate are all insoluble in excess; Cd, Bi white, Hg<sup>ic</sup> brown, with excess yellow and in presence of ammonia, white; Cu, light blue, on boiling black.

The iodides, see 23, 11. Wet way reductions (20, 6) show best in reflected light under the microscope: Bi acicular gray, Cd mosslike gray; Cu mosslike red crystals. See also pyrognostics.

Bi solutions give white turbidity with water, not soluble in tartaric acid, only soluble in mineral acids. Copper solutions, even if extremely dilute, give a brownish precipitate with Ka Cy<sup>o</sup> Feate solutions.

5. THE SILVER GROUP reacts towards H Side and yellow ammonium sulphide exactly as the copper group, from which it differs by being precipitated by H Cl<sup>ide</sup> or any other soluble chloride. See 22, Note 1. Iodides, see 23, 11.—Ka Crate precipitates Ag deep purplish red; Hg<sup>ous</sup> brick red; Pb bright yellow, soluble in Ka Hate, but difficultly soluble in dilute nitric acid. Ka Hate precipitates the hydrates: Ag, light brown, Hg<sup>ous</sup> black, both insoluble in excess (Ag Hate soluble in aqua ammonia to explosive compound); Pb white, soluble in excess, no immediate precipitate in presence of acetic acid. Pyrognostic, see 53.—Wet way reductions, very fine: Ag, arborescent, white crystals; Pb, acicular gray crystals; Hg, on copper, silvering, volatilized by heat.

6. THE ZINC GROUP is not precipitated by H Side gas in acid solution, but like the aluminium group, precipitated thereby in alkaline solutions; it is distinguished from the aluminium

group by its hydrates being soluble in sufficient Am Cl<sup>ide</sup> solution. The pyrognostic tests on charcoal and borax beads are specifically distinctive (Lect. 53). Mn on soda bead, GREEN mass (manganate) dissolves in acid solution to purplish permanganate.

Potassium hydrate precipitates all, an excess dissolves Zn only; from this solution, H Side reprecipitates the Zn, but Am Cl<sup>ide</sup> does not (distinction from Al). The Mn precipitate, white, turns dark brown; Fe<sup>ous</sup> white, turns promptly greenish, then rust brown; Ni light green, unchanged, dissolved by Am Cate to greenish blue solution; Co, blue precipitate, turns green, on boiling reddish, is soluble in Am Cate to brownish red solution.

Fe<sup>ous</sup> solutions, even if extremely dilute, are precipitated deep blue by Ka Cy<sup>i</sup> Feate (red prussiate of potash), while the Ka Cy<sup>o</sup> Feate (yellow prussiate) give bluish white precipitate, turning gradually deep blue in air.

7. THE ALUMINIUM GROUP is characterized as just stated under 6, its hydrates being insoluble in Am Cl<sup>ide</sup>. The precipitate with H Side in alkaline solutions is the hydrate, not a sulphide. See 22, 10.

Ka Hate gives a precipitate in all cases: Al, white, readily soluble in excess, reprecipitated by Am Cl<sup>ide</sup>, not by H Side (distinction from Zn); Cr<sup>ic</sup> greenish, soluble in excess, reprecipitated by Am Cl<sup>ide</sup> OR by protracted boiling; Fe<sup>ic</sup>, brown precipitate, not soluble in excess.—See Pyrognostic reactions, Lect. 53, and group tests, Lect. 22.

Ferric solutions, even if extremely dilute, give with Ka Cy<sup>o</sup> Feate the deep blue precipitate (Prussian blue), insoluble in H Cl<sup>ide</sup>, readily soluble in Ka Hate.—With Ka Cy<sup>i</sup> Feate, no precipitate. With Ka S-Cyate, deep blood red coloration, destroyed by Ka Acetate, restored by H Cl<sup>ide</sup>; color dissolved in ether. Extremely sensitive reaction. Cr compounds, fused with soda and nitre on loop, give chromate, yellow.

8. THE BARIUM AND MAGNESIUM GROUPS remain in solution, if the treatment with H Sate (Lect. 22) has been

omitted. In the case of mixtures, it is best so to do; but in case of presence of phosphates, the previous precipitation as sulphate has advantages.

If no sulphate has been added, the second group (Ca, Sr, Ba) is precipitated as  $\text{C}^{\text{ate}}$  in the first reaction of VIII; the precipitate removed by filtration, the precipitate may be tested for members of second group by flame (53, 3) and spectrum (52, 6) while the filtrate is worked up as directed in Lect. 22, Note 5.

9. THE PRESENCE OF PHOSPHATES, oxalates, silicates, borates and fluorides, singularly complicates the analytical separation of the last two groups (our II and VIII). When the solution is made alkaline, previously to the precipitation of the zinc and aluminium groups, such phosphates, etc., of the barium group go down, and will be found in the precipitate of VI, VII. By means of  $\text{Ba C}^{\text{ate}}$  a separation is effected, but the operations are too complicated for the present.

10. SEPARATION of the different groups is effected by the group reactions given. Separation of members in a group depends on the individual characters given in this lesson. Thus  $\text{Fe}^{\text{ic}}$  is separated in VII from Al by  $\text{Ka H}^{\text{ate}}$ ; Cd and Cu from  $\text{Hg}^{\text{ic}}$  and Bi in III by excess of  $\text{Am H}^{\text{ate}}$ ; Pb from Ag and  $\text{Hg}^{\text{ous}}$  in I by water, and Ag from  $\text{Hg}^{\text{ous}}$  in the washed precipitate by  $\text{Am H}^{\text{ate}}$ . Such work, however, is specially restricted to the Laboratory Stands.

## 55. WET WAY ANALYSIS OF ACIDS.

1. Having found the metallic constituent (27.5) in the given compound, the known SOLUBILITY of the compound examined will often enable us to exclude quite a number of acids or non-metallic constituents, so as to limit our search to those possibly present.

2. Thus, if LEAD has been found in a compound soluble in water, it cannot possibly be the carbonate, sulphate, chro-

mate, sulphide, oxide, chloride, iodide; for these lead compounds are all insoluble in water, as may be remembered from previous lessons. If the lead compound examined had been insoluble in water, any of the above acids might be present, but nitrate and acetate could not be, since lead nitrate and acetate are soluble in water.

3. Accordingly it is important to be able to tell what compounds are soluble in water, and which are insoluble therein. For neutral compounds, the following simple RULES OF SOLUBILITY will answer all practical purposes:

4. SOLUBLE are nearly all the salts of Na, Ka and Am; also Nitrates, Chlorates and Acetates.

SOLUBLE are the Carbonates, Phosphates, Silicates and Oxalates of Na, Ka and Am.

SOLUBLE are the Hydrates, Oxides and Sulphides of Na, Ka (Am) and Ca, Sr, Ba.

INSOLUBLE are the Sulphates of Ca, Sr, Ba and Pb; the Chromates of Ba, Pb, Ag, Hg, Bi.

INSOLUBLE are the Chlorides of Ag, Hg<sup>ous</sup> Pb; also the Iodides of same and of Hg<sup>ic</sup> and Bi.

5. Those non-metallic constituents which yield a gas (EFFERVESCE) upon the addition of a non-volatile acid, will have been detected while testing for groups I and II (p. 146). If the effervescence is odorless, and yields turbidity with lime water, it is a carbonate. If the effervescence exhibits the odor of burning sulphur, it is a sulphite; rotten eggs, a sulphide; peach blossoms, a cyanide.

6. Chromates, Manganates, Permanganates, Arsenates and other salts containing a heavy metal and forming METALLO-SALTS reveal themselves by a separation of sulphur (p. 146.3) when the acid solution is saturated with hydrogen sulphide gas. At the same time, the color of the solution often changes. Thus Chromates, being yellow or red, change to green; Manganates are green and turn brownish; Permanganates turn from purplish to brownish.

7. If the non-metallic constituent has not been indicated by these reactions made in the course of examination for the metal, the following REAGENTS are used: Ba Nte, Ca Sate and Ag Nate, detecting respectively Sulphate, the Phosphate group and the Chloride group. If no precipitate obtained, the Nitrate group is present.

8. If the original solution acidified with nitric acid gives a precipitate with Barium Nitrate, the compound is a SULPHATE. This precipitate, taken up in a soda bead, and exposed to the inner flame of the blowpipe, will stain a silver coin black upon the addition of a drop of water or muriatic acid, under the evolution of hydrogen sulphide gas, readily recognized by its odor. This is the so-called hepar test.

9. If the neutral or slightly alkaline solution of the substance examined yields a white precipitate with Calcium Sulphate, the PHOSPHATE GROUP of acids is present. If the precipitate upon the addition of acetic acid dissolves, it is a phosphate (compare p. 146, 5-6); if it does not, it is an oxalate. The other acids (Silicate and Fluoride) are most readily detected in the dry way (10.5; 11, 4).

10. If no precipitate yet obtained, another portion of the original solution is acidified with nitric acid and a few drops of silver nitrate are added; a curdy precipitate indicates the CHLORIDE GROUP. The precipitate is separated and washed by decantation, and treated with strong ammonium hydrate, to ascertain whether the curdy precipitate is soluble or not therein. In the latter case, it is an IODIDE.

11. If soluble, it is either BROMIDE or CHLORIDE (for cyanide would have been detected in 5). If the original solution with chlorine water turns yellowish, and if upon shaking with chloroform this turns orange while the aqueous solution becomes colorless, a bromide is present; if not, the substance is a chloride.

12. If no precipitate so far obtained, the given compound is a Nitrate, Acetate Chlorate or Borate. An excess of concen-



trated sulphuric acid being added: to one portion add copper turnings, rutilant vapors prove the Nitrate; to another add a few drops of alcohol, the odor of acetic ether indicates acetates. If neither of these, add a drop of concentrated sulphuric acid to a small fragment of the substance - yellow, chlorous gas evolved proves the CHLORATE.

If no such odor or gas, try flame coloration; if outer mantle green, the substance is a BORATE.

If all these reactions failed to give a positive result, the substance is an oxide or hydrate, to be recognized by its physical characters.

## 56. RECOGNITION OF SPECIMENS.

1. This concludes the introduction to inorganic chemistry. If this course has been complemented by laboratory work, the student now is fairly familiar with the most important SUBSTANCES, FACTS AND PRINCIPLES of inorganic chemistry.

2. He will have acquired the important ability of the RECOGNITION OF SPECIMENS of minerals and chemical compounds, mainly by their physical properties, but aided by simple chemical tests made either by the blowpipe, or by a drop of a dozen or two of reagents applied to the minute sample in a watchglass or on a microscope slide.

3. The MICROCHEMICAL REAGENTS for this sort of testing in the wet way are kept in small bottles with pipette and ground glass cap, or cork stoppered, the stopper carrying from below a short piece of glass rod dipping in the liquid. Of course, the drop taken must be placed on clean glass, near the drop or substance to be acted upon, to prevent contamination of the reagent. By a working glass rod the mixture is effected.

4. The necessary SULPHURETTED HYDROGEN GAS is generated in a test tube, broken below, divided into two equal compartments by a perforated cork disk, and inserted into a

cylinder or salt mouth flask with dilute muriatic acid. The tube is held at any desired depth by means of a cork wedge. The upper compartment contains a couple of pieces of iron sulphide, and is closed by a cork, through which passes a glass tube connected with rubber tube and spring clamp. To the rubber attach the delivery tube.

5. Depressing the tube starts the GENERATION OF THE GAS, only a few bubbles of which are required at a time. When not at work, be sure to have the cork partition a centimeter above the level of the acid. Such a little apparatus is a perfect substitute of the Kipp generator for the elementary microchemical work here contemplated.

6. THE TABLES given in this text (Lectures 22, 53, 54, 55), are sufficient for the beginner. A minute fragment of the solid is all the MATERIAL REQUIRED for testing. A few watch glasses and microscope slides take the place of the test tubes, beakers and flasks. A few pieces of hard (Bohemian) glass tubing and an alcohol lamp (glass) will permit to add dry way work. The work is most interesting and instructive.

7. FOR EXAMPLE, a small prismatic crystal is given for recognition. A portion thereof, in a watch glass, dissolves readily in a drop of water. Dots made with this solution are placed on a microscope slide (or slides). With  $H\ Cl^{ide}$  and  $H\ Sate$ , no Pr; these with the sulphide gas give Pr, first y, then bn, finally bk; Pr with drop of water, run off, leaves residue insoluble in drop of yellow  $Am\ Side$ ; evidently  $Hg^{ic}$  compound. Confirm by  $Ka\ loide$ , Cu, etc.

Excluded are acids:  $Cate$ , etc.;  $Hate$ , etc.;  $Crate$ ,  $loide$ . No effervescence, no volatile acid. Dot acidified with a touch of dil.  $H\ Nate$  gives no Pr. with  $Ba\ Sol$ ;  $Pate$  group excluded on account of insolubility; another acidified dot with a touch of  $Ag\ Nate$  gives white curdy Pr—readily sol.  $Am\ Hate$ , hence either  $Cl^{ide}$  or  $Br^{ide}$ , since  $Cy^{ide}$  proved absent— $Br^{ide}$  test made in watch glass with single drops shows no  $Br^{ide}$  reaction. Hence, crystal was  $Hg^{ic}\ Cl^{ide}$ , CORROSIVE SUBLIMATE.

8. RECOGNITION OF COMMON MINERALS should be practiced on small fragments, and cleavage pieces; the greatest dimension need not exceed one centimeter, so that a large number of specimens can be given in a small paper tray or an ordinary specimen tube. Hardness should be determined by the nail, copper, glass and file. Gravity need not be actually determined, if blowpipe or microchemical tests applied, or if the work is restricted to the most common minerals.

9. If determinations of the specific gravity are wanted, make a HYDROSTATIC BALANCE, by replacing one horn pan of the common German hand scale by a double pan of wire gauze held about 8 or 10 cm. apart by brass wires; the lower of these pans being submerged in the water of a small crystallizing dish. For weights, use common block weights from 10 gr. to 1 cgr. Weigh specimen in air on upper, in water on lower wire gauze pan.

10. CLEAVAGE pieces frequently permit good determinations by means of our goniometer, p. 68. Thus Barite and Celestite give right rhombic cleavage pieces. For Barite the angle of the prism is less than 102 degrees (11, 9); but for Celestite this angle is 104 degrees, a difference easily recognized. In fact, Haüy distinguished these mineral species by this notable difference, before strontium was known, a feat comparable to modern distinctions by spectrum lines. (*Traité*, T. 2, 318-326; Paris, 1801).

11. A DIAGRAM on which the leading mineral species are located according to their G and H as horizontal and vertical dimensions, (co-ordinates) is very useful for the recognition of minerals. Thus, at about H 6 and G 5 are located three species only, namely Pyrite, Hematite and Magnetite. But the first is readily distinguished by its brilliant metallic luster and yellow color (9, 8), while the last two are distinguished by their streak (9, 6).

12. On such a diagram, the species of a genus form some definite curve, showing that the PHYSICAL PROPERTIES ARE

DEFINITE FUNCTIONS OF THE METAL. Thus the sulphates  $R O_4 S$  in which  $R$  is  $Ca$ ,  $Sr$ ,  $Ba$ ,  $Pb$  form the definite curve parallel to and a little below the curve for the corresponding carbonates  $R O_3 C$ , which are about half a degree harder. The author has found work of this character far superior to the common study of systematic chemistry.

## 57. ORGANIC PRIME MATERIALS.

1. Minerals constitute the body of the earth. Together with the water of the ocean and the gases of the atmosphere, they have furnished the prime materials for our chemical investigations. Thus far, we have studied inorganic chemistry only.

2. Under the action of the light and heat of the sun upon the air and moisture, the surface of the earth has been covered with plants. Attached to the mineral world by their roots ramifying in the soil, they push stem and branches up into the air and unfold their leaves to the sunbeam which every season calls forth flowers and fruits as the highest forms of **VEGETABLE MATTER**.

3. Almost every portion of vegetable matter is utilized by animals as food. To secure this, animals are endowed with a power of voluntary motion. Vegetable matter is transformed by the animal into bone, muscle and nerve; also into egg, blood and milk. Such substances are **ANIMAL MATTER**.

4. The whole earth becomes more and more the **GARDEN OF MAN**. "Out of the ground grow trees pleasant to the sight and good for food." Man is getting a more complete "dominion over the fish of the sea, over the fowl of the air, and over every living thing that moveth upon the earth." But the earth "brings forth thorns also and thistles," so that "man eats his bread in the sweat of his face." Genesis, 1-3.

5. Plants and animals furnish the prime materials for organic chemistry, as minerals do for inorganic chemistry. ORGANIC CHEMISTRY, in its broadest sense, treats of the changes of matter of the organic world.—1. 5-7.

6. The starchy grain, when germinating, becomes soft, sweetish, gummy; a new plant grows from it. In the leaves of this new plant we notice green coloring matter, woody cell tissue, acids; at least during flowering, volatile substances are formed; then new grains make their appearance, at first gummy, then sweetish, finally starchy. Such a cycle of changes is a subject for investigation in organic chemistry; its LABORATORY IS THE CELL, its power, the Sun.

7. This new grain, mixed with malted barley, changes to a sugar; exposed to the ferments of the air, it produces alcohol; this is readily converted into thousands of new materials, such as acetic acid, aldehyd, chloral, chloroform and ethers. Many such processes have for centuries been practiced on a large scale; they are OPERATIONS OF ORGANIC CHEMISTRY.

8. Organic matter contains carbon, as is readily shown by the simple test of charring (1, 5), which also generally permits us to distinguish animal from vegetable matter. Accordingly, modern chemists have defined organic chemistry as the chemistry of carbon compounds, ostensibly to maintain the unity of the science of chemistry; but the innovation is rather narrow.

9. As a matter of fact, the products of the soil throughout the world and their modifications by animals furnish almost exclusively the PRIME MATERIALS OF ORGANIC CHEMISTRY. In the economy of nations, these products alone are of importance. To increase their production, to improve their quality, and multiply their forms of application, marks the main working field of organic chemistry. In this field the United States are prominent.

10. In the course of the chemical changes of these prime materials, many NEW and valuable PRODUCTS are obtained, first in the laboratory and afterwards in the factory. But in nearly all cases, these new substances either are identic with or correspond to substances furnished by plant or animal, and often were already used by the ancients.

11. This is especially striking regarding the COAL-TAR PRODUCTS, the investigation of which has, in some regions, almost monopolized the efforts of the chemist. This inevitable one-sidedness has led to systematic errors, and boastful assertions of superiority as unfounded as they are unbecoming.

12. Hasty conclusions, unwarranted generalizations and bulky publications have marred the work of the last quarter century. THE CHEMICAL PRESS has become rather sensational, not merely in its diagrams and long names. In real science, we need more earnest thought, less haste; more grain, less straw in our publications. In our industry and intercourse, less of the modern "survival of the fittest," a heartless philosophy of doubtful foundation; more of a revival of the moral code and the golden rule.

## 58. SUGAR AND WINE.

1. The tall SUGAR CANE has its home in Asia (India and China). The Arabs planted it in Italy and Spain. Since it has found its most extended cultivation in America, from Cuba to Brazil. The juice (90 per cent.) of the ripe cane is sweet; it is a strong solution (10 to 18 per cent.) of true sugar, the SUCROSE of modern chemistry.

2. The juice is pressed out by passing the cane between revolving cylinders. Gentle heating with a little lime removes impurities. Concentration in (open and vacuum) pans gives crude sugar in crystals, and molasses. In the refineries of Europe and the United States (14, 11), the pure, crystallized

sugar is obtained. Tropical America produces one and one-half million tons. Asia, Africa and Australia one million tons. Total, two and one-half million tons of cane sugar a year.

3. SUGAR (sucrose) is a white solid without odor. G 1.6; F 160, solidifying to a white, amorphous, vitreous mass, gradually becoming opaque and again crystalline. At higher temperatures it chars and burns.

Sugar is soluble in half its own weight of cold water, and in all proportions in hot water. From its solution it crystallizes in oblique rhombic prisms (M M' 101.5 and M P 98.5) called Rock candy. The Maple sugar of New England is also mainly sucrose.

4. The same sugar (sucrose) was discovered by Marggraf of Berlin in the juice of the beet (1747). About 1830 France had 50 beet sugar factories; twenty years later the beet sugar production had taken root in Germany and Austria. These two countries now produce two million tons of BEET SUGAR, while the balance of Europe produces one and one-half million tons only. Total, three and one-half million tons of beet sugar a year (1889-90).

5. Honey and Manna were the only SWEET SUBSTANCES known in antiquity, even to the Greeks. The Hindoos had extracted sucrose from the cane, 500 B. C. The Arabs brought sucrose to Southern Europe. With the importation of slaves, cane planting began in tropical America. During the last forty years, chemistry has profoundly modified agriculture in Central Europe, which now extracts more sucrose from the beet root than is produced in the sugar cane of the tropics.

6. States, recognizing the economic advantages of increasing and diversifying the industries, have at all times fostered new industries by SPECIAL LEGISLATION. The history of the beet sugar industry shows the marvellously stimulating effect of such legislation, but also the depression that seems an unavoidable sequence. Europe now is in the latter stage,

while we are entering upon the first stage by voting a bonus upon the production of all sugar.

7. Ripe GRAPES taste sweet; but no sucrose can be extracted from them. When dried (raisins), the sweet principle appears as a gritty solid, called grape sugar or GLUCOSE. It promptly reduces the boiling Fehling-Solution (an alkaline tartrate of copper) giving a red precipitate of cuprous oxide. A fresh sucrose solution gives no precipitate; hence the importance of this test. Figs and many other fruits give the same reaction; so does honey; they contain glucose.

8. When ripe grapes are piled up, they burst under their own weight; the rich, sweet juice or must (95 per cent. of berry) runs out. Set aside in filled vessels, it undergoes a remarkable change, called FERMENTATION, during which much fixed air (16.8) is given off. Finally, the liquid becomes clear again: it is WINE, the special product of the white race, the milk of old age that ought to be but sparingly used by the young.

9. WINE MAKING is probably the oldest chemical industry. The patriarchs made wine and drank it. The Egyptian monuments show the cutting of the grapes from the trellises, and the pressing of the must. The Greeks and Romans held wine in high esteem. Among modern nations, the French produce the most, over 2,000 million gallons a year before the phylloxera came, and about 800 million gallons a year during the last 10 years. Spain, Italy and Germany come next. In America, California has long been foremost, both in amount (12 million gallons) and quality of the wine produced.

10. Slow distillation of wine yields a very volatile liquid, known in the 13th century as AQUA VITÆ and used as a medicine, to which the most extravagant virtues were ascribed. This is our brandy. The finest is produced in France (Cognac). California also manufactures good brandy in large quantities. Its specific gravity should range between 0.92 and 0.94. It is readily inflammable, burning with a pale blue flame, leaving a liquid residue.



11. Subjecting brandy to fractional distillation, the most volatile fractions become lighter and more completely combustible (spirits). When the specific gravity is reduced to about 0.82, the liquid is properly called ALCOHOL. By careful distillation it can be brought down to 0.81. When distilled from quick lime (after a day's contact therewith in a closed vessel), the distillate may be brought down to 0.79, boiling at  $78^{\circ}4$ . This is ABSOLUTE ALCOHOL, solidifying at  $-130$  degrees. It is extremely hygroscopic.

12. The alcohol of 0.82 contains 94 per cent. of absolute alcohol by volume, 91 per cent. by weight; the STRENGTH OF AN ALCOHOL, containing only water as diluent, is determined by its specific gravity, 47, 11.

Alcohol is PRODUCED (for industrial purposes) in enormous quantities from various sources in these days. In the year 1890-91, Germany produced 75 million gallons, France 50, Russia 100, Austro-Hungary 50, England 25; total 300 million gallons (of 100 per cent.) or a million gallons a day. The production of the United States is also very great.

## 59. FATS AND OILS.

1. The basin of the Mediterranean Sea, the seat of civilization of antiquity, is the home of the olive tree. The Greeks regarded it as a symbol of peace, a gift of the Gods. Its wood is hard, growth slow, size moderate, foliage elegant, flowers delicate, white and fragrant, fruit fleshy, containing half its own weight of the purest fatty oil, yielding to simple pressure: OLIVE OIL. It is yellowish, G 0.915, and begins to solidify at  $5^{\circ}$ .

2. The portion of olive oil remaining liquid at the freezing point is called OLEIN; it amounts to about three-fourths of the oil. The last traces of the solid constituent of olive oil are removed by repeating the process.

Olein remains liquid on exposure to the air; it is a non-drying oil. It congeals at  $-6$  degrees, is soluble in ether and in boiling alcohol. Rutilant vapors solidify it; this solid (elaidin) melts at  $32$  degrees.

3. The solid residues of sweet oil are, by pressure, freed from the olein adherent, the last traces of which are extracted by boiling alcohol; what remains is called PALMITIN or margarin. Crystallized from ether, it melts at  $61$  degrees, but may be cooled to  $41$  degrees before it solidifies again. Accordingly, sweet oil is a mixture of about three parts of olein and one of margarin. These two fats are also the constituents of the fat of the human body.

4. The hunter and herdsman obtained the fat required for food from the animals he captured or raised. The best, most readily digested fat, is BUTTER; it is also the most complex, so that its consideration must be deferred for the present. By melting on a water bath, animal fats are obtained in the purest form; especially TALLOW, melting at  $45-46$  degrees, from the ox; LARD, ( $38-40$  degrees) from the hog, and SUET ( $50$  degrees) from the sheep. Goose grease melts at  $25-26$  degrees; it does not deserve the neglect it receives in modern medicine, which prefers inert, non-assimilable petroleum products.

5. When cold lard is subjected to hydraulic pressure, LARD OIL runs out and a white solid, STEARIN, remains.

Lard oil is produced in enormous quantities in America; it has the general properties of olein, but betrays its hog-origin by instantly producing reddish-brown color in contact with concentrated sulphuric acid. This coloration is evidently due not to the main body of the lard oil, but to an ingredient present in small amounts only.

6. The solid fat STEARIN is obtained pure by pressing purified suet at  $25$  degrees, dissolving the residue in its own volume of hot ether, from which stearin crystallizes on cooling. These crystals are purified by pressing, and recrystallization.

Stearin melts at 70 degrees; it is but little soluble in alcohol and ether at common temperatures; it freely dissolves in boiling ether. Suet contains one-fifth olein; the balance is margarin and stearin.

7. FATS FROM FISH are generally recognized by their odor. A single whale (physeter) will furnish 80 tons of whale oil, mainly consisting of two liquid fats, olein and physetolein. Cod Liver Oil is extracted from the liver of *Gadus Morrhua* and kindred species of *gadus*. It consists mainly of olein; owes its reputation to ingredients present in minute quantities, and not yet fully known. A drop of concentrated sulphuric acid produces a series of colors resembling the strychnine color reaction. See 64, 11.

8. Linseed yield upon pressure a fixed oil which, on exposure to the air, dries to a varnish. It contains about 20 per cent. of solid fats; no olein, but the liquid, drying linolein instead. Accordingly, it does not solidify with rutilant vapors. By boiling with litharge, the drying qualities of the oil are improved.

9. In general, fatty substances are greasy to the touch, and non-volatile, leaving on paper a permanently transparent spot. They are lighter than water (on which they float); G 0.90 to 0.94. At common temperatures they are either solid (FATS) or liquid (OILS). They may be separated by cold and pressure into a few simple fats of perfectly definite properties (stearin, margarin, olein). They are insoluble in water, partly soluble in (hot) alcohol, readily soluble in ether. They are combustible; when incompletely burnt they emit a characteristic odor (acrolein). When kept exposed for a long time, they become rancid (odor).

10. Before the war, cotton seed was a waste product in our southern states. Now, the COTTON SEED OIL adds materially to the profit of the planter. Enormous quantities are produced; much goes to the packing establishments of this country, and "over six million gallons are shipped annually to

Mediterranean ports contiguous to the olive oil industry" (Remington). Alcoholic silver nitrate solution, shaken with cotton seed oil, and heated, tinges the oil red or reddish-brown.

11. The fact is, lard oil, cotton seed oil and olive oil consist mainly of olein and margarin in similar proportions. By density and solidification they can not be distinguished. It is true, lard oil produces a COLOR REACTION with sulphuric acid and cotton seed oil another with silver nitrate solution; but these tests indicate the presence of an impurity that may be removed. Of course, good cotton seed oil is a good oil, and will bring a good price sold under its own name.

12. To conclude the identity of these oils is manifestly absurd. The constituents present in minute amount, the combinations breaking down before our reagents, often are the most valued, to say nothing of the history or provenance of the material. The "artificial wine" may yield the same analytical results as a true wine; yet the maker of the first is condemned in Germany, where the latter brings a high price. Frauds in oils and fats are frauds; where chemistry fails to detect it, the brand of an honorable firm will protect the consumer and the producer.

## 60. FLOWER AND FRAGRANCE.

1. Its highest form of beauty and fragrance, the vegetable world has produced in THE ROSE. Though in the lower sense "useless"—offering nothing for the stomach—the rose has ever been held in the highest estimation by man. Hundreds of varieties have been produced by culture; but the old centifolia and damascena are among the richest in fragrance.

2. In the Orient, the culture of the rose has remained economically prominent in numerous localities. The country about Kisanlik, in Bulgaria, largely supplies the market with the OIL OF ROSE, in which the subtle fragrance is concentrated in a permanent form. This oil, quoted at about a dollar

a drachm, represents fully three thousand times its own weight of the delicate rose petals. It is a pale, yellowish, transparent liquid (G about 0.87 at 20 degrees), congealing between 16 and 21 degrees to a transparent solid with many slender, shining crystals.

3. The oil of rose is obtained by distilling rose petals with water; the oil floats on top of the distillate. VOLATILE OILS, even if of much higher boiling point than water, are readily carried over with the large excess of water vapor in this process of distillation, which is quite generally employed for the extraction of the fragrant principles of plants. In some districts this ATTAR is distilled without the addition of water to the petals, the latter containing a sufficiency for the purpose.

4. Many of the most beautiful and FRAGRANT FLOWERS are grown on a commercial scale in favored regions in the open, and throughout the civilized world under glass, to supply the demand in the immediate vicinity for the flower. Floriculture has enormously increased during the last quarter century. Florists have also learned to ship their perishable products long distances, as from Sicily to England.

The southeastern corner of France, with Nice as the commercial center, is the most remarkable flower garden of modern times. The country, gently sloping towards the sunny Mediterranean, is completely protected by the Maritime Alps against the chilling winds of the north. From this favored region, fresh flowers are shipped to the north—as far as England—during the winter, and the fragrance of flowers is extracted on a large scale throughout the year.

5. The finest and most delicate fragrance of flowers suffers to an appreciable extent by the process of distillation with water. For such flowers, the process of ENFLEURAGE has been devised, in which the purest fats (lard), spread in thin layers on glass frames, absorb the fragrance of the flowers at common temperatures. The flowers are laid or sprinkled on these "chassis," of which a number are piled to a stack. In from 6 to 12 hours the fats have absorbed all the fragrance;

the exhausted flowers are removed and replaced by fresh ones till the fat is saturated.

6. This POMADE is the commercially permanent form in which the concentrated fragrance of the flower is shipped throughout the world. The largest establishments of this manufacture are at Grasse, about 15 miles west of Nice. This industry is strongly marked by peculiar characters for which French industry is noted. In a very small bulk, an immense amount of skilled labor and scientific thought has been condensed; a very small weight brings the producer a very large sum of money.

7. The receiver—retailer—of these pomades, cuts them into small pieces, and shakes these with the proper amount of purest alcohol, which dissolves the fragrance, forming the so-called ESSENCE of the flower; the fat being insoluble in alcohol, is removed by decantation (best after standing in the cold). It is only when properly diluted that the real fragrance is brought out.

8. Algiers, Australia and the United States have made a good start in this interesting and profitable field. The peppermint culture and industry of Michigan has attained a controlling influence in the market. The OIL OF PEPPERMINT is distilled with water from the leaves and tops of *Mentha piperita*, gathered before flowering. The oil (G 0.91) has "the characteristic odor of peppermint; a strongly aromatic, pungent taste, followed by a sensation of cold when air is drawn into the mouth."

9. The small evergreen shrub, rising at intervals from the creeping root of *Gaultheria procumbens* yields, upon the distillation of its oval, leathery leaves, the OIL OF WINTER-GREEN, the heaviest of all volatile oils (G 1.18, B 218-221). It is colorless or yellowish, and has a strong specific odor, a warm aromatic taste; it is soluble in alcohol; when shaken with water, a deep violet color will be produced upon the addition of a drop of ferric chloride.

10. An "ARTIFICIAL" or "synthetic" oil of wintergreen has been put on the market; being made from "synthetic" salicylic acid, obtained from coal tar, it is profitably supplied at half the price of the genuine.

The "artificial" is in no sense chemically identical with the genuine; it is not even a safe "substitution." But it is declared to be as good as the genuine, and that it has driven the genuine out of the market, so that even "salicylic acid made from oil of wintergreen" is no longer genuine. "If cheaper and better," it ought by all means to be sold under its own name. Such a condition is deplorable, demoralizing. It can be met by a reliable "brand" only. See 59.12.

11. Several volatile oils are obtained BY EXPRESSION, notably the oils of bergamot, of orange peel and of lemon peel. For further details, special treatises must be consulted about this entire subject.

The pure volatile oils make a STAIN on paper; but this stain completely disappears on exposure, while the stain made by fatty oils is permanent.

12. From peppermint oil separates a crystallized solid, called MENTHOL (G —, F 43, B 212), volatilizing considerably at common temperatures. The Japanese oil is particularly rich in menthol, which first reached us from Japan.

CAMPHOR (G 0.995, F 175, B 204), distilled with water from the wood of the camphor tree of Formosa, is similar to menthol, but has been long in use. Its odor is characteristic and well known.

## 61. INDIGO AND MADDER.

1. The vegetable world presents in its flowers all the colors of the rainbow; it also shows rich color in fruit and foliage, and even in wood and root. Man has tried to extract and employ these colors; but the tints of the petals have almost invariably proved too dainty for his hands. From the other

parts of the plant, SUBSTANTIAL COLORING MATTERS have been obtained.

2. Already in antiquity, these colors were transferred to the vegetable fibre by which man protected and adorned his body. The oldest part of the Scriptures speak of GARMENTS DYED in red, purple and scarlet. The heros of Homer wore purple. The dyers of Tyre and Sydon were famous. The Egyptians, as Pliny reports, understood the use of mordants, apparently as well as we do to-day.

3. INDIGO is one of the oldest vegetable colors; it has been in use at least three thousand years, and is as important to-day, as ever. Eight thousand tons of indigo, worth over twenty million dollars, are produced annually, mainly, in India, its home, whence Alexander brought it to Greece as indian (indicon) blue. In naming the substance we state its origin.

4. The plant, *indigofera tinctoria*, shows no blue coloring material. Shortly before flowering, the plant is cut off, thrown into great vats with water and lime; a sort of fermentation sets in, the coloring material passing into solution. This greenish-yellow solution is drawn into lower vats, beaten with bamboos for hours to introduce air; now a blueish sediment settles to the bottom—it is the CRUDE INDIGO, about one fifth of one per cent of the plant taken.

5. The crude indigo of commerce contains several coloring principles. Its percentage of true indigo is extremely variable, ranging from 20 to 90. The deep blue lumps show a reddish streak. PURE INDIGO is obtained by mixing the pulverized crude substance with its weight of pulverized glucose, dissolving in alkaline alcohol. The yellowish solution is decanted; upon exposure to the air indigo gradually precipitates, and after washing with dilute muriatic acid, is pure.

6. PURE INDIGO BLUE is a blue, tasteless (crystalline) solid, insoluble in water, alcohol, ether, acids and alkalies, slightly soluble in chloroform, glacial acetic acid and spirits of turpentine, from which solutions it separates in acicular crys-



tals. When carefully heated, it forms a sublimate of red acicular crystals; its vapors are purplish red. It is soluble in fuming sulphuric (Nordhausen) acid. In reducing alkaline liquids it dissolves to a colorless liquid, indigo-white (Chevreul, p. 37); on exposure to the air it returns to indigo-blue or true indigo. This explains the common method of dyeing with indigo.

7. India is also the home of *rubia tinctorum* (MADDER), the root of which has served from time immemorial as the principal red dye. From the Orient, the culture of madder reached Europe in the 17th century, and became specially prominent in southern France. Since 1869, this old industry has almost disappeared, not only from France, but also from Asia Minor and other countries, to the great loss of the populations affected.

8. The pulverized madder, treated with its own weight of sulphuric acid, gives a blood red mass, the garancine of the French. Exhausting this with boiling alcohol, the cooling liquid deposits yellowish brown acicular crystals of ALIZARINE and purpurine. Both are soluble in a boiling solution of alum, from which alizarine precipitates on cooling. This is the coloring principle of madder.

9. The reddish yellow crystals of PURE ALIZARINE melt at  $215^{\circ}$ , volatilize between this temperature and  $240^{\circ}$ ; they can be sublimated in a porcelain crucible heated on a sandbath. Alizarine is scarcely soluble in water, moderately soluble in boiling water and in alcohol. It dissolves in sulphuric acid, which it colors blood red. Its alcoholic solution is turned violet by alkalies; lime turns it blue. A hot alum solution dissolves it; on cooling, it precipitates in crystal form.

10. In 1869 the German Chemists, Graebe and Liebermann, succeeded in producing alizarine from anthracene, one of the least volatile constituents of coal tar. Their method was unpracticable, however. The English Chemists, Caro and Perkin, soon after, devised a chemical method both simple

profitable. Since then, ALIZARINE IS MADE on a large scale FROM COAL TAR, and the madder culture has been ruined. France used to export six million dollars worth of madder; now Germany produces that much alizarine from coal tar.

11. The two vegetable colors presented are TYPICAL of this important class of bodies. Many lessons, economic as well as scientific, can be drawn from what has been stated.

In conclusion, the economic value of colors extracted from woods (logwood, etc.), may be estimated from the fact that Europe, in 1888, imported two hundred thousand tons of such woods from the tropics, representing about eight million dollars in value.

12. The most important vegetable color of all has not been mentioned yet; it is CHLOROPHYLL, the green color of leaves. It is insoluble in water. but soluble in alcohol, and especially in ether. By frost it is decomposed into red and yellowish tints, so admirably exhibited by American forests in the fall season. In spring, more delicate tints mark the swelling and opening buds—but require more attention to be seen.

## 62. BALSAM AND RESIN.

1. We read of “wise men from the East” having been miraculously guided by a star to the new-born King; “and when they had opened their treasures, they presented to him gifts: gold, and frankincense, and myrrh.” This is a formal recognition of the estimation in which Orientals hold choice resins and balsams—treasured with gold.

2. Modern man looks down upon such customs as manifestations of ignorance and superstition—and then dives into the TAR PIT, applies all his powers and extracts by highest chemical art “new” substances of wonderful properties, makes the use of these products almost compulsory to cure and prevent disease, and to preserve food from corruption ’till needed for strength.

3. And lo! these vaunted NEW SUBSTANCES owe their value exclusively to their correspondence with the exudations of the fragrant shrubs and trees of India, Arabia and Africa, used and prized from time immemorial by our superstitious ancestors who, however, were not ignorant enough, by such substances, to make their food indigestible. The Egyptians preserved their lifeless bodies, but they did not embalm their food.

4. BENZOIN is a balsamic resin, obtained from *Styrax Benzoin*, a tree at home on Sumatra and Java. Alcohol dissolves most of its active principles. When moderately heated, it yields a crystallized aromatic sublimate, insoluble in water, but soluble in sodium carbonate with effervescence, and re-precipitated by sulphuric acid. The sublimate, accordingly, is a true acid; it is called benzoic acid.

5. Scheele (p. 169) made use of the wet way reactions just stated to extract pure benzoic acid from benzoin.

When the acid is heated in a distilling apparatus with three times its weight of slacked lime, a colorless distillate is obtained, called BENZOL (Mitscherlich, p. 34). This substance is the starting point of all aromatic compounds. We give the characteristic of these two bodies.

6. BENZOL is a colorless, very limpid liquid of a characteristic odor. G 0.90 at 0, F 0°, B 80.4; crystallizes in rhombic octahedræ. Insoluble in water, soluble in alcohol and ether. Is a good solvent for iodine, sulphur, phosphorus, camphor, wax, fats, and india rubber. It burns with a fuliginous flame.

7. BENZOIC ACID (Equivalent 122) is a white solid, forming pearly scales or silky needles; has a slight aromatic odor of benzoin, and a warm, acid taste; acid reaction. F 121, B 250. Very slightly soluble in cold water ( $\frac{1}{300}$ ), moderately soluble in boiling water ( $\frac{1}{15}$ ), quite soluble in alcohol, ether, chloroform, benzol. Freely soluble in aqueous solutions of alkalies, forming soluble salts.

It begins to sublime at  $100^{\circ}$  already, and freely passes over with vapor of water. Neutralized solutions give a flesh colored precipitate with ferric chloride.

8. We have no balsam trees in the North, but possess immense pine forests which impregnate the air with their peculiar aroma—both healthful and pleasant. The wood is rich in an oleoresin (TURPENTINE), to obtain which the great pine forests of our Southern States are now being devastated by “turpentine orchards.” The turpentine industry is old in the Carolinas. Southwestern France also produces turpentine, but not in that ruthless manner.

9. When turpentine is distilled with water, OIL OF TURPENTINE forms a layer on the water passing over. The volatile oil may be rectified from lime water.

Oil of turpentine is a thin, limpid, very volatile, colorless liquid, of a characteristic odor and taste, neutral reaction (becoming faintly acid by exposure to the air). G. 0.86 to 0.87. Insoluble in water, soluble in thrice its volume of alcohol. It acts on bromine or iodine with explosive violence; in contact with a mixture of nitric and sulphuric acid, it inflames. Its vapors mixed with air explode on ignition.

10. The residue left of the turpentine after distilling is called colophony. It is a true resin, being readily soluble in alcohol, and entirely insoluble in water.

COLOPHONY is a transparent, amber colored solid, hard, brittle, with conchoidal fracture, showing the typical resinous luster; it has a faint terebinthine odor, and is inflammable. G 1.07 to 1.08, F 135. Solubility as stated above; also readily soluble in ether, fixed and volatile oils.

11. Oil of turpentine, when distilled in vacuo or in an atmosphere of fixed air, is destitute of odor. Exposure to the air reproduces the odor, which accordingly is due to the oxidation of the oil, which thereby is resinified. All volatile oils seem to possess this peculiarity. In the same manner, pure arsenic distilled in fixed air has no odor; it exhibits the characteristic garlic ODOR ONLY WHILE BEING OXIDIZED.

12. Turpentine yields about one fifth of its own weight of volatile oil, leaving four fifths of resin. Such bodies are named OLEO-RESINS. GUM RESINS consist of a gum (soluble in water, insoluble in alcohol) and a resin. Myrrh and asa-foetida are examples. Balsams are resinous substances containing benzoic acid or similar aromatic volatile solids. Styrax, balsam of Tolu, balsam of Peru, may be mentioned in addition to benzoin described.

### 63. VEGETABLE ACIDS.

1. Goethe voiced the longing of the children of the North for the "Sunny South," the land where the lemon trees are in bloom, and where through the dark foliage the golden ORANGES glow. Nevertheless, the Northern APPLE orchard in full blossom at the coming of the summer season, and loaded with luscious fruit at its close, we deem the more beautiful of the two. It was an apple, not an orange, that tempted the mother of us all.

2. Chemically, both the lemon and the apple furnish us typical ORGANIC ACIDS, namely citric and malic acids. SCHEELE, that marvellously skillful chemical worker, has taught us how to extract these acids. Though a century has elapsed, we cannot do better than follow his directions (p. 169).

3. While climatic conditions limit the habitat of the trees producing these REFRESHING FRUITS, the almost ripe fruit is sufficiently resistant to stand shipment to distant countries. Thus Italy and California supply the world with lemons and oranges, while our Northern States send apples to Europe by the million barrels.

4. THE JUICE OF THE LIME contains more citric acid than the lemon and largely supplies the growing demand for this acid. After freeing the juice from mucilage by a beginning fermentation, it is saturated with chalk, the precipitated

calcium citrate washed with boiling water and treated with dilute sulphuric acid. The resulting citric acid solution is drawn off from the precipitated gypsum and concentrated to crystallization.

5. CITRIC ACID occurs in colorless, translucent, right-rhombic prisms, not deliquescent in dry air; odorless, agreeable acid taste. Freely soluble in water, less so in alcohol. It gives no precipitate with lime water except on boiling; the precipitate redissolves on cooling (if an excess of lime water was used).

The crystallized acid (equivalent 70) begins to lose water (of crystallization) at about 75; melts above 135, and decomposes at a red heat, without emitting the odor of burnt sugar.

6. The acid which Scheele in 1785 extracted from the apple (*pyrus malus*) he called MALIC ACID. He found the same acid in cherries, currants, blackberries, strawberries and other fruit. The barberries, the berries of sumac (*rhus glabra*) and of the european mountain ash are especially rich in this acid. It also occurs in rhubarb and tobacco.

7. These berries of the mountain ash are gathered before they are fully ripe. The juice is expressed, and clarified by being brought to a boiling (albumin). The filtered liquid is boiled with milk of lime, giving a deposit of neutral calcium malate. After washing, this deposit is added, in small portions at a time, to boiling dilute nitric acid; the acid malate so formed crystallizes on cooling. These crystals are treated with lead acetate, the lead malate precipitated is suspended in water and treated with hydrogen sulphide gas. The filtrate yields, on careful evaporation, deliquescent crystals of malic acid.

8. MALIC ACID (equivalent 67) occurs in acicular crystals, forming mamellary groups; it is deliquescent, very soluble in water and in alcohol. F 100. It begins to decompose at 120 degrees.

Malic acid gives no precipitate with lime water, neither hot nor cold. Calcium chloride gives no precipitate, except upon boiling. This precipitate, dissolved in the least amount of hydrochloric acid, is reprecipitated by alcohol.

9. Scheele separated several other organic acids by his methods, namely: the formation of the calcium salt from which the organic acid is set free by dilute sulphuric acid under the separation of insoluble gypsum, or the formation of the lead salt, from which the lead is separated by hydrogen sulphide. In addition to the preceding acids, he extracted especially oxalic and tartaric acids in this way.

10. OXALIC ACID is extracted from various species of sorrel (oxalis), generally containing the potassium salt. The acid is now made in quantity from starch or from sawdust.

Crystallized oxalic acid (equivalent 63) is quite permanent in air (24.10) and moderately soluble in water. Calcium compounds give a crystalline precipitate, insoluble in acetic or oxalic acid, but soluble in muriatic acid. See p. 146, 5, a; 55,9.

11. Potassium tartrate is contained in the ripe grape, and insoluble in alcohol; it therefore separates as tartar (argol) during fermentation. This is dissolved in dilute muriatic acid, and saturated with chalk. The precipitated neutral calcium tartrate is washed and treated with dilute sulphuric acid; the filtrate is carefully evaporated (best in vacuum pan) to crystallization.

12. TARTARIC ACID (equivalent 75) forms colorless, odorless, monoclinic crystals, permanent in air. F 135, decompose at higher temperature, emitting the odor of burnt sugar. Soluble in water, less so in alcohol.

The acid gives a crystalline precipitate (cream of tartar) with potassium acetate, insoluble in acetic acid, readily soluble in alkalies and in mineral acids.

## 64. VEGETABLE BASES.

1. The strange potency of many plants had become familiar to man long before historic times. The myths of Hekate, daughter of night, and of her high walled garden full of POISONOUS PLANTS, are sufficient evidence. Concordant

herewith, modern explorers have found most savage races in possession of poisons and narcotic remedies.

2. Even the SPECIFIC ACTION OF POISONS was known to the ancients, partly studied by experiments on condemned criminals or slaves. The most famous instance of this knowledge we read in Plato's account of the tests made by the executioner on Socrates, verifying his prediction of the action of the fatal cup by which the civilized Greeks relieved themselves of their greatest teacher.

3. Besides, most races of men have become addicted to the use of some potent plant as STIMULANT OR NARCOTIC. Poppy in the eastern hemisphere, Tobacco in the western world. Tea in China, Coca in South America; Coffee in Abyssinia, Chocolate in Mexico. The pure wines of the Ancients of our own race have been fortified in the destructive spirits manufactured by their descendants.

4. The dominant race, in its conquest of the continents of the West and South, PAYS TRIBUTE to China for tea, to America for tobacco, and has planted the coffee tree wherever it will grow. The cultivation, transportation and distribution of these apparently useless plants has become an important factor in the economy of nations. In reality they must supply a legitimate want.

5. The remarkable action on the system, depending in its character on the amount taken, has always been well known, but too often disregarded. In MINUTE DOSES, strychnine is a valuable remedy, but already half a grain may kill under horrible convulsions. Opium, in small doses, relieves the sick of pain; habituation to larger doses, stupefies the mind and kills the body. These substances evidently are like knives and guns, requiring skill and understanding for their proper use.

6. Many of these active vegetable materials have never been employed except as remedies. The bark of the CINCHONA trees of the Andes were so used against fevers by the



natives, who imparted this knowledge to their conquerors. The process of gathering the bark (p. 52) being destructive, cinchona plantations have been established in the Dutch and English colonies of India. Rational cultivation and harvest now supply the valued bark at reasonable rates.

7. Until 1817 the active principles of these remarkable substances remained unknown. FREDERICK SERTUERNER, a pharmacist of northwestern Germany, had already in 1805 separated the "principium somniferum" of opium, the inspissated juice of the poppy, and also extracted, by Scheele's process, meconic acid from the drug. But hardly any attention was paid to his results 'till in 1817, he published his method of extracting morphine from opium.

8. Sertuerner treated opium with dilute acetic acid, precipitated the filtered solution with ammonia, and purified the precipitate by crystallizing it from its solution in hot alcohol; this substance he called MORPHINE. It forms white, slender prismatic crystals, permanent in air, very bitter; scarcely soluble in water, ether or benzol, moderately soluble in alcohol, especially when warm, and readily soluble in purified fusel oil.

Morphine crystals are identified by turning orange red with nitric acid, and blue with neutral ferric chloride.

9. THIS MODE OF EXTRACTION proves morphine to be a base, brought into solution by acetic acid, and precipitated by ammonia because it is insoluble in water. With acids it forms definite salts, generally soluble in water, from which they can be obtained in crystal form. They are insoluble in most organic solvents. Resembling the alkalies, morphine is called an alkaloid.

10. Nearly all the plants referred to above contain active principles of this kind, or ALKALOIDS. They are EXTRACTED from the crude drug by a like process, modified according to the special solubility of the alkaloids; they are distinguished or IDENTIFIED most generally by some specific color reaction. This important subject can hardly be studied with profit except in the laboratory course.

11. *Nux vomica* contains the alkaloid STRYCHNINE, very soluble in chloroform. It is identified by remaining white (colorless) with concentrated sulphuric acid, and striking a deep blue color with a crystal of potassium bichromate, drawn through the acid film covering the strychnine crystals. This blue color almost instantly changes to deep blueish violet, which gradually passes into an indefinite reddish tint. See 59, 7.

12. The ALKALOIDS of tobacco (nicotine) and of hemlock or conium maculatum (coniine) are VOLATILE liquids; hence they can be obtained by distilling the drug with dilute potassium hydrate. The impure distillate, made alkaline with potassium hydrate and shaken with ether, will yield the alkaloid on spontaneous evaporation of the ethereal solution. Coniine is distinguished by its strong, mousy odor. Hemlock infusion was the poison cup of the Greeks; see 2.

## 65. NEUTRAL PRINCIPLES.

1. Many plants yield to neutral solvents, such as water and alcohol, crystalline substances destitute of marked acid or alkaline properties; such substances are called neutral principles. Some of these principles resemble alkaloids, others seem to act like acids. Most have a marked taste, especially bitter or astringent, and some act powerfully on the system (cathartics).

2. THE BARK OF THE WILLOW imparts an intense red color to sulphuric acid. Poured into water, the diluted acid gradually becomes colorless, depositing a dark red precipitate. These reactions are due to salicin, which may be extracted by boiling the bark with milk of lime, evaporating the clear, decanted solution to dryness, and exhausting the residue with weak alcohol; the salicin will crystallize after the alcohol has been distilled off.

3. SALICIN crystallizes on cooling from hot solutions in water or in alcohol, forming white, silky needles, permanent in the air; it is odorless, very bitter; its solutions have a neutral reaction. F 198. It has been used as a febrifuge.

It is identified by the above given reaction with sulphuric acid and water. Heating a small portion with the chromic oxidizing mixture (bichromate and sulphuric acid), the characteristic odor of the oil of meadow sweet (*spiræa ulmaria*) will be noticed.

4. When salicin is boiled with dilute sulphuric acid, the solution will, after neutralization, give the glucose reaction with Fehlings reagent (58.7); accordingly, glucose has been formed from salicin. Special researches have shown that there also forms the compound, saligenin, and that water has been taken up. Substances which take up water and yield glucose, are called GLUCOSIDES.

5. The flower heads of *Artemisia pauciflora* are sold under the name of Santonica (Levant Wormseed). Mixing the ground "wormseed" with slacked lime, and exhausting the mixture with hot water, the concentrated filtrate yields crude SANTONIN as precipitate on the addition of muriatic acid. The product may readily be purified and crystallized from alcohol. It turns yellow by exposure to light. It acts like a feeble acid. It is a noted anthelmintic.

6. The kernel of *Cocculus Indicus* is bruised and extracted with hot alcohol; this solution is concentrated to a thick, syrupy consistence (removing separated fat). Boil the residue with water, filter, and set the hot filtrate aside for crystallization. The crude crystals, purified by recrystallization from alcohol, are PICROTOXIN. It is a bitter glucoside, extremely poisonous.

7. The inspissated juice of the leaves of several varieties of Aloes are quoted in the drug market under the name of Gum Aloes. When Barbadoes aloes is treated with ten times

its own weight of water (slightly acidified with muriatic acid), the liquid decanted after cooling, and evaporated to about double the weight of the gum taken, crystals will slowly form (in a week or two). This is ALOIN (barbaloin). It is extremely bitter; in small doses (2 cgr) a laxative, in larger doses (10 cgr) a cathartic.

8. The inner bark of *Quillaja Saponaria* of South America contains the glucoside SAPONIN, which is extracted by hot water. Its aqueous solution froths when agitated, like soap-suds; the froth is very slow to settle. Medicinally it is an irritant diuretic; technically it is used to cleanse silk. It is also used as an adulterant to foaming liquids.

9. THE TANNING OF HIDES to form leather is one of the oldest industries. The cleaned animal hide decays (putrefies) rapidly; but if packed in white oak bark, it slowly changes to leather, which is quite permanent in both air and water.

The active principle of the oak bark is called tannin. It is best extracted from nut galls, which contain fully half their own weight of tannin.

10. Powdered NUT GALLS are extracted in various ways with water and ether; the water dissolving the tannin, the ether taking up the impurities from the solution. The liquids are separated, the aqueous solution concentrated and spread to dry on glass or tin plates to obtain the TANNIN as a yellowish, non-crystallizable powder. It is very soluble in water and dilute alcohol, but almost insoluble in absolute ether.

11. The taste of tannin is strongly astringent. Its solution precipitates most solutions of animal materials, especially gelatin and albumin; hence its use in tanning. It also precipitates most salt solutions, and forms with ferric solutions a black precipitate; ferrous solutions turn black on exposure to air (INK). Tannin acts like a feeble acid, but has been generally considered a glucoside.

12. Aqueous solutions of tannin, exposed to the air, undergo GALLIC FERMENTATION, due to the presence of the complex

ferment *penicillium glaucum*. Glucosides present yield glucose which, after the gallic fermentation is completed, give alcohol.

Tannin is one of the most common vegetable products, contained in most barks and leaves. It is recognized by its astringent taste and its reaction with ferric solutions or with gelatin.

## 66. STARCH AND FIBER.

1. Thus far we have by the simplest methods possible extracted our organic prime materials from plants, especially by pressure, heat and solvents. The insoluble residue left in all these cases constitutes the main body of the plant. This resistant material gives each plant its characteristic form. It is called woody fiber or CELLULOSE.

2. The microscope shows the wood cell to be essentially cylindrical in form, varying greatly for different tissues in the same plant and for corresponding tissues in different plants. By treating the crushed and broken tissue in succession with the solvents used to extract the vegetable principles studied, the WOODY FIBER will remain as a white, fibrous mass, insoluble in water, alcohol, ether, dilute alkali and acid.

3. This woody fiber may be extracted from almost any plant with more or less labor; we find it, however, quite pure in COTTON, the fiber of which, under the microscope, appears as twisted ribbons. The so-called absorbent cotton is obtained by removing the small amount of fatty material present in raw cotton. Linen, the smooth, round fiber of flax, is also very pure cellulose.

4. In wood proper, the true cellulose is thickened with LIGNIN, which is brittle. It can be removed by treating the properly divided wood with lime saturated with sulphur dioxide under pressure (2 to 3 atmospheres). This gives the WOOD-

PULP, so much used for lower grades of paper, and largely imported from Norway and Germany. Phloroglucin and concentrated muriatic acid turn lignin intensely purple-red; hence white paper can be tested for lignin by this reagent.

5. Cellulose can be dissolved by Schweizer's reagent; an ammonical solution of cupric hydrate. Cellulose is re-precipitated by acids, forming a white amorphous powder, purified by washing with alcohol.

Some animals (Ascidia) contain a corresponding material Tunicin (animal cellulose); in its solubilities it closely resembles true cellulose.

6. THE IMPORTANCE OF CELLULOSE TO MAN can hardly be expressed in words. Man has dressed himself in linen and cotton; coarser fibers he uses for sacks and cordage. When these are worn out—rags—he makes paper thereof. Of the wood itself he builds houses and ships, and also burns it for comfort and power. But above all, woody fiber gives form to plants—the beautiful mantle of the globe.

7. If we examine a thin slice of almost any tuber or seed, we find the cells of the tissue to contain smaller globular cells, called STARCH. If the ground or crushed material is washed on a sieve or straining cloth, the starch runs through the cloth with the water, and gradually settles in the receiving vessels.

8. STARCH GRAINS show concentric layers around a nucleus (hilum) in the center or near one end of the grain. The form, while in the main globular, shows specific modifications for each plant, as well as characteristic dimensions, so much so that in many cases the plant can be named from a microscopic examination of the starch.

9. POTATO starch is the largest (60 to 100 microns), somewhat egg-shaped, the excentric hilum and rings readily distinguished. RICE starch is among the smallest (3 to 7 microns), the grains showing polygonal forms. WHEAT starch

(20 to 30 microns), is larger than CORN starch (15 to 20 microns); the former is spherical, the latter somewhat polyhedral. A micron is the thousandth part of a millimeter; it is the unit of microscopic measures. 2, 5.

10. STARCH is insoluble in (cold) water, but soluble in strong solutions of zinc chloride, calcium chloride and similar salts. Starch is also insoluble in alcohol.

When starch is heated with water, the grains swell and burst, giving, on boiling, starch paste. Alcohol precipitates herefrom soluble starch as a white powder, soluble in cold water. In the paste, the membranes remain as shreds; the cell-contents (granulose or amidin) only has dissolved. Iodine is a most delicate reagent for starch (23.4).

11. Starch, being one of the principal constituents of FLOUR, is a valuable food. The roller process—like the mill stones of the ancients—crushes the grain without tearing it; but excessive bolting produces a very white, insipid flour containing an undue proportion of starch. Potatoes are the poorest, wheat is the most nutritive; corn contains most fat, rice the least of fiber.

12. STARCH being required in many industries (textile, paper, glucose) it IS MANUFACTURED in enormous quantities. In Germany starch is largely extracted from potatoes; in Russia, from wheat; in the United States, from corn (maize), and in England from (imported) rice. From the tropics we get arrow-root and genuine sago, which resembles potato starch somewhat; accordingly the tuber sometimes is sold where the palm is called and paid for.

## 67. MILK AND BUTTER.

1. Milk is the food of all young mammals; to man it is a valuable food throughout his entire existence. The most abundant and cheapest source is THE COW (p. 49); the best product is obtained from cows in good pasture. "The old

pastures" on which no plow has drawn furrow for centuries, extending on the west coasts of Germany from Holland to Sleswig, and protected by dykes from the sea, furnish milk in flavor and richness unsurpassed.

2. THE PRODUCTION OF MILK occupies a prominent place in the economy of nations. The entire money value of the production of gold is insignificant when compared to the market value of the golden butter produced throughout the world in the same time—and yet butter is only one of the products of milk, though the one that most extensively enters commerce.

3. MILK is chemically a very complex liquid, and in its nature PERISHABLE. After evaporation in vacuum pans, with the addition of sugar, it can be shipped far and kept for a long time. By freezing it has also been shipped, especially from Denmark to England. But the most rational course consists in the shipment of the two most valuable and permanent products, butter and cheese, and to use the balance for food on the farm.

4. THE PROXIMATE ANALYSIS of milk has been practiced from time immemorial; upon it rests the milk industry. By simply allowing milk to stand in a cool place, its lightest parts, CREAM, rise to the surface, forming a layer of about one-tenth the depth of the milk. This cream, after ripening, yields BUTTER by simply churning. The skim-milk, on spontaneous or artificial acidification, yields CASEIN (cheese); the whey left gives, upon concentration, milk sugar (LACTOSE) in crystals, and SALTS (potassium phosphate, chloride) as residue.

5. By the introduction of modern CENTRIFUGAL SEPARATORS, the stream of fresh milk flowing into the machine comes out in two continuous streams, namely, the lighter cream from the inner, the heavier skim-milk from the outer sheet. The Laval separator makes fully one hundred revolutions a second, thus instantly separating milk into its two layers for which the less intense gravity requires twenty-four hours.



6. The microscope shows that milk is an (opaque, white) EMULSION; a transparent, aqueous solution holding minute fat (BUTTER) GLOBULES in suspension. These globules are each covered with a thin film, which readily yields to alkalis, after which the ether will dissolve the fat and leave it upon spontaneous evaporation. While not the most exact, this is the most instructive determination of the per cent. of butter in milk.

7. By such processes it has been ascertained that GOOD COW MILK contains about 13 per cent. of the four solids constituents specified; the balance (87 per cent.) being water. The percentage of the four solids averages as follows: fat, 4 (butter); sugar, 5 (lactose); curd,  $3\frac{1}{2}$  (casein), and salts,  $\frac{1}{2}$ . Human milk contains about one per cent. more of sugar (6) and one per cent. less of casein ( $2\frac{1}{2}$ ); it is more sweet and much more easily assimilated than cow's milk.

8. FRESH MILK is sweet and faintly alkaline; G 1.03. By exposure it becomes acid; LACTIC ACID forming (best between 25 and 35 degrees). In proportion as this acid forms, the casein is precipitated (coagulated). After straining and washing, this CRUDE CASEIN may be purified by dissolving it in a strong solution of sodium carbonate at a moderate temperature. After removing fats, and other impurities, the casein may be obtained by precipitation with an acid, and washed with water, alcohol and ether.

9. CHEESE consists mainly of the casein of milk. If made from skim-milk, the cheese is hard, almost like a brick; it is said, "dogs bark at it, hogs grunt at it, but neither dare bite it." Made from whole milk, it retains all the fat, and is both palatable and nourishing. By various additions and peculiar processes of ageing, numerous varieties of cheese are produced. Some districts are famous for their special brands of cheese that bring deservedly a high price in the market.

10. BUTTER is the most complex and the most easily assimilated fat known; hence the high price it brings, and

hence also the multiform attempts to imitate it. Genuine butter has a specific aroma and rich golden color; G 0.94, F 31, solidifying at 20. It contains 56 per cent. solid fats (stearin and palmitin), 36 per cent. of olein, and 8 per cent. of butyrin with certain other light fats and flavoring ingredients well known to the connoisseur, but not scientifically defined.

11. The real VALUE OF BUTTER depends upon the judgment and taste of the consumer; if the consumer does not know good butter from indifferent or bad, or genuine from spurious, he will be satisfied with the low grades and imitations. The chemist can only detect rather glaring frauds. When we come to the study of the fatty acids, we shall learn to understand this.

12. Since 1870, the market is flooded with ARTIFICIAL BUTTERS, including ox-butters, hog-butters and worse. The term butter having an established signification, its use for any chemical imitations is in its very nature fraudulent; legislation, even in Germany, is now beginning to recognize this fact. But specially feeding cows low grade fats (cotton seed oil cakes, etc., etc.) adds to fraud the contemptible attempt to make the innocent cow a particeps criminis.

## 68. FLESH AND BLOOD.

1. The highest material life on the globe is represented by the warm blooded animals. Man has taken their flesh as food; first as a hunter, next as herdsman, and now as farmer. The domestic animal occupies a conspicuous and most important place, both in the permanence of soil fertility and in the immediate financial rewards. THE WEALTH OF modern NATIONS, as was that of the patriarchs, is largely represented in the number of their cattle.

2. The primitive process of drying, salting and smoking, permit the PRESERVATION OF perishable MEATS beyond the

day of procurement and thus also their entrance in the commerce of the world. The modern process by refrigeration permits transcontinental and oceanic shipment of so-called "fresh meats;" but the product suffers really more than by the older methods. It has built up great trusts, depressed both local industry and agriculture, and is fast depriving the rising generation of the knowledge of genuine beef.

3. The old sage said BLOOD IS THE LIFE OF THE FLESH (Gen. 9, 4); modern investigations have fully substantiated this statement. Blood is the most wonderful liquid of nature. Our scientific methods are crude when applied to this liquid; in modern days we have, through the investigations of PASTEUR (p. 31) and his disciples, obtained many demonstrations of the Mosaic statement.

4. BLOOD is a most complex liquid,  $G\ 1.05 - 1.07$ ; its odor is specific, varying with the animal. In every (warm blooded) animal blood presents two strikingly different modifications: bright red in the arterial system, flowing from the heart to the substance of the flesh, and darker, blueish in the return current of the venous system. Each of these modifications shows its own specific absorption spectrum between D and E (52, 12).

5. A small drop of blood, spread out by the cover glass, shows under a good microscope, a multitude of minute disk-like GLOBULES or CORPUSCLES. In human blood there are about five millions of globules to the droplet (of one cubic millimeter), each globule being 8 microns in diameter and 2 microns thick. In most mammals the globules are also circular disks. In birds, reptiles and fishes their form is elliptical, and often much larger than in man. In frogs their larger diameter is 22 microns.

6. Freshly drawn blood, left standing in a glass cup, gradually separates into the semi-solid, red CLOT and the pale-yellow liquid SERUM. The clot (on washing) leaves white FIBRIN; in the water the globules settle like starch. The

serum will also coagulate when exposed long enough. Human blood contains 12.7 per cent. of globules, and 0.3 per cent. fibrin in the clot, and 7 per cent. albumin in the serum; total 20 per cent. solids, and 80 per cent. water.

7. Serum, when gently heated, coagulates; the whitish solid is mainly ALBUMEN. The white of eggs shows the same deportment to heat. The albumens are distinguished as egg- and serum-albumen. They differ slightly, especially in their resistance to a rise in temperature. Egg albumen coagulates more readily (at a lower temperature) than serum-albumen. Methods of purification cannot here be given.

8. The blood globules are covered with a thin fibrinous membrane, and consist of red HÆMOGLOBIN and the albumen-like substance globulin in the proportion of about 8 to 1. Hæmoglobin is the real coloring matter of the blood. Shaking fresh blood in a flask with a small amount of ether, the globules are broken up; when the flask is set aside for a night in the cold (best in melting ice) crystals of hæmoglobin will be found on the walls of the flask. The crystals contain iron.

9. A dilute aqueous solution of hæmoglobin ABSORBS OXYGEN gas, and becomes brilliant red, showing two dark absorption bands one each near D and F. Any REDUCING GAS drives out the oxygen, the color changes to that of dark blood, and a broad absorption band appears midway between D and E, instead of the two bands characterizing the red or oxyhæmoglobin. These changes can be exhibited repeatedly in succession.

10. The blood also contains MINERAL MATTER, left upon incineration. The clot gives mainly iron and potassium compounds; both leave phosphates and chlorides. The serum gives sodium salts.

Salt solutions exert a remarkable effect on blood. Blood run into ten times its own volume of a 2 per cent. salt solution does not coagulate; the globules settle to the bottom of this mixture.

11. The muscular tissue is built up from blood; the muscular fiber is related to fibrin. Again, the used up parts are removed by and in the blood, partly serving a further purpose in the hepatic system (BILE) in aid of digestion, partly being removed through the kidneys (URINE), skin (PERSPIRATION) and lungs (RESPIRATION). We shall very briefly consider the chemical processes involved in a subsequent lecture.

12. Albumen, fibrin and casein, as well as their modifications, are called albuminoid substances, also PROTEIDS, nitrogenous substances, plastic food, etc., etc. Singeing them, they emit the characteristic odor (1, 5). They are extremely prone to change. We distinguish them mainly by their most common mode of solidification or coagulation; albumen by heat, casein by acids, and fibrin by mere exposure to the air.

## 69. BONE AND SINEW.

1. The deep contains animals depending on the surrounding medium for support and even form; their body consisting of flesh and blood only. But all higher animals, from the fish of the sea to the bird of the air, have their flesh connected by strong SINEWS to a frame work of BONES, whereby they show infinitely varied beauty of form and perfection of mechanism.

2. The dominant form of bone is the TUBE. Galilei has shown this form to be the most economical, giving the greatest possible strength for the amount of material employed. The material itself is also most perfect, being a living tissue of mineral ( $\frac{2}{3}$ ) and organic ( $\frac{1}{3}$ ) matter, possessing both STRENGTH AND ELASTICITY in a high degree.

3. The mineral matter of a bone is dissolved in dilute (10 per cent.) muriatic acid in the course of a few days. The liquid shows mainly calcium phosphate (85 per cent.) and

carbonate (11 per cent.); the balance being about equally calcium fluoride and magnesium phosphate. The well washed organic material, OSSEIN, retains the form of the bone used, but is flexible and elastic, so that it may even be tied in a knot.

4. Boiling ossein in water, converts it into GELATIN, which is soluble in hot water, but solidifies to a jelly upon cooling. When the gelatin solution is so dilute that it does not set to a jelly on cooling, an aqueous solution of tannin will give a most characteristic, white flocculent precipitate. Alcohol also precipitates dilute solutions of gelatin.

5. The white fibers of connective tissue (sinews and tendons) are mainly composed of COLLAGEN, that is, a substance which changes the gelatin when boiled with water. When connective tissue is treated with acetic acid, the white fibers swell up and become transparent, while the elastic fibers (elastin) remain unchanged and can be seen distinctly under the microscope.

6. Gelatins of greatly varying qualities are manufactured, bringing correspondingly different prices. From the low grades of GLUE, the prices run up to divers fine brands of GELATIN for culinary purposes and for clarifying liquids. The purest and most costly is the genuine Russian Beluga ISINGLASS, made from the swimming bladder of certain sturgeons.

7. When these gelatins had first been extracted, especially from bones under pressure, they were recommended by chemists as cheap and good foods for the poor. These foods were introduced into penal and charitable institutions, to the great disgust of the inmates, whose unsophisticated stomachs were denounced as prejudiced, till the rats in a raid ate all in sight but this "bone soup." GELATIN IS NO FOOD.

8. The substance of horn and hoof, feathers and hair, and of the epithelial tissues generally, are less soluble and contain sulphur; when boiled with water under pressure they yield

sulphuretted hydrogen. These substances are called KERA-TINS. From feathers, a brownish-yellow keratin is prepared for coating pills. Such pills are not acted upon in the stomach, and permit the introduction of remedial substances to the intestines.

9. SILK, the most costly fiber, is manufactured by the silk worm from mulberry leaves. It consists of a smooth, round, thread (fibroin) covered with sericin or silk-glue. The latter is readily dissolved by soap solutions to a sort of glue, while the former resists; both are rapidly dissolved by alkalies, but are much less acted upon by acids. Silk is very hygroscopic. An "artificial silk" is made from collodion.

10. Bones burnt in an open fire leave about two-thirds of white BONE-ASH. This is used for cupels (7.6) and for the extraction of phosphorus. This method of extraction was first devised by Scheele. By sulphuric acid much lime (as gypsum) is removed from the bone ash; the phosphate solution is evaporated to a syrup, and in two stages reduced by charcoal.

11. Bones heated with exclusion of the air leave BONE BLACK or animal charcoal, and yield an offensively smelling distillate, Dippel's oil. The charcoal results from the organic material, the ossein, and retains all the mineral matter. Animal charcoal is a most important absorbent for coloring and odoriferous substances, and hence constantly used as filter for organic liquids in the laboratory and in the arts (sugar refineries).

12. Animal charcoal, having been used, may be REVIVED by first washing it out and then charring it again. This process is even repeated, on account of the high price of the material. When finally no longer fit, even as admixture to fresh animal charcoal, it may be used as a source of phosphorus. Bones are also utilized by first extracting the fat with benzol, then the ossein with water, and lastly, the phosphorus as indicated above.

## 70. ANIMAL AND PLANT.

1. We have seen in what manner the principal prime materials of organic chemistry are extracted from plants and animals, and how they are purified. They yield chemical compounds of perfectly definite chemical and physical properties.

2. Before we begin a more detailed study of the chemical transformation of these prime materials, it will be advisable to look upon their mutual relations in the GREAT CIRCLE OF MATERIAL LIFE. Air, water and soil we shall find to be the substances, sunshine the power, and the living cell the laboratory in which this chemical circulation of matter takes place.

3. PLANTS GROW from seeds. These seeds are very small compared to the plant. The substance of the oak was never contained in the acorn. Burning the wood of the tree, we obtain heat (FIRE) as power, also carbon dioxide and water as material products disappear in the atmosphere; finally a few per cent. of mineral matter (ASHES) remain as visible solids of the wood burned.

4. This rapid destruction (combustion) of the plant we now know to be the exact opposite of its slow growth. The SUN supplies the heat necessary to unite aqueous vapor and carbon dioxide of the AIR to the combustible material of the plant under separation of oxygen gas; the soil supplies the MINERAL MATTER remaining in the ashes.

5. Numerous LABORATORY EXPERIMENTS on growing plants in glass cylinders, permitting an accurate determination of the changes effected on the air supplied, have proved this. The effects of mineral matter have been specially studied by growing plants (beans, indian corn, etc.) in dilute solutions of accurately known mineral composition (Sachs), confirming the earlier chemical results (Liebig, p. 23) on ashes and soils.



6. That growing PLANTS EXHALE OXYGEN GAS can readily be seen by examining the gas accumulating over any green foliage under water and exposed to the sun light. A simple funnel suffices to hold the foliage. The gas accumulating in the stoppered neck of the funnel re-kindles a glowing shaving when the stopper is withdrawn. It is oxygen.

7. The comparatively small amount of nitrogenous material produced in the plant (especially stored in its seeds) has been traced, in like manner, to the AMMONIA of the air and in the soil. Hence the beneficent effects of animal manures. The fertility of the soils of Europe is sufficiently enhanced by guano to warrant the importation thereof from the opposite extremity of the globe.

8. The herbivorous and grain eating animals depend for their food entirely on the plants; even carnivorous animals do so, because their prey subsist on plant food. But animals require equally a pure air, rich in oxygen, for respiration. Without VEGETABLE FOOD, animals slowly starve to death; without OXYGEN, they die promptly from suffocation.

9. Throughout the system of the animal, the absorbed vegetable food (chyle) and the oxygen of the air unite chemically; the red blood becomes dark from the products of this combination. In the LUNGS the carbon dioxide is sent back to the atmosphere (16. 9). In the KIDNEYS the products of the combination of nitrogenous substances or proteids are separated (urea, uric acid). The SKIN largely removes the water in perspiration. Undissolved food RESIDUES are evacuated as feces.—See blackboard diagram.

10. The union of the vegetable food with the oxygen of the air throughout the system constitutes a real wet-way combustion, and produces the HEAT AND MUSCULAR POWER of the body. The first experimental researches in this field were made by Lavoisier (p. 19). Grimaux has published two most instructive plates in his *Life of Lavoisier*, showing these remarkable experiments.

11. It is evident that animal life contains within itself the CAUSES OF ITS OWN DESTRUCTION or death. The air exhaled poisons the atmosphere. In a like manner, the other products of animal life are poisonous to such life. While plants are less sensitive, vegetable life alone would also produce conditions destructive to itself.

12. Thus, not only does animal life depend upon plants for food, but even for constantly destroying the poisonous effects of animal life on itself and its surroundings. In a like manner animal life makes it possible for vegetation to flourish. The two forms of life supplement each other to one grand circle of chemical and physical transformations, depending for its permanence on that of the sun.

## 71. FERMENTATION AND LIFE.

1. Bread and wine have nourished and refreshed man from the earliest times. Both substances involve chemical processes of great mystery. The grain and the grape furnished by plant-life, have undergone an additional chemico-vital process before they became fit for food. This process is FERMEN-TATION.

2. Moses prohibited the use of leavened bread during the exodus. It was also prohibited in burnt meat offerings. These are probably the oldest historic records of LEAVEN. The wonderful rapidity wherewith "a little leaven" changes a large amount of meal, is used repeatedly as a striking figure in the new testament. The fermentation of grape juice was practiced as far back as the flood.

3. Van Helmont (p. 30) is the first modern investigator who reached a fair conception of the importance of fermentation in the economy of nature; he rightly compared VITAL PROCESSES in health and disease to fermentation. The microscope afterwards showed the presence of special cells in

leaven and ferment. But even Liebig (1870) considered these cells non-essential to the chemical process going on.

4. It is PASTEUR (p. 31) who has discovered the true function of ferments in nature's household. In fermentation we have the life process of the cell. The ferment cell feeds on glucose; the products of its vital act are carbon dioxide and alcohol. To grow, the ferment cell requires nitrogenous food and salts, as do higher plants. Pure glucose solution will not ferment.

5. THE GERMS of ferments float in the air. Solutions, sterilized by boiling in glasses loosely stoppered with cotton, will not ferment; the germs possibly present being killed by the heat, and germs from the air being stopped by the cotton. Even a downward bent neck prevents the germs from falling into the flask. There is no spontaneous generation. Thus Pasteur in the sixties.—Tyndall strikingly showed the germ filtering effect of cotton on air. The nose is such a germ filter for our own lungs.

6. The most common ferments for wine, beer and bread are globular or elliptical, acting on the saccharine substances; hence they are called SACCHAROMYCES. The beer yeast contains the *S. cerevisiae*, consisting of almost spherical cells, growing by budding while young, forming nuclei when old (see plate). The wine ferment, *S. ellipsoideus*, is named after the elongated form of its cells.

7. At common temperatures (16 to 20 degs.) beer wort ferments rapidly, the yeast rising to the SURFACE. At lower temperatures (6 to 8 degs.), the wort ferments slowly, requiring weeks instead of days; the yeast collects at the BOTTOM. The beer produced in the latter case is called lager. The ferment of surface fermentation differs from that of bottom fermentation. Both are present—but each grows best at its own temperature.

8. Beer or light wine exposed to air becomes sour; acetic acid is formed, due to the growth of *BACILLUS ACETICUS*,

which thrives best (optimum) between 18 and 35 degrees, and requires air (aërobic ferment). The souring of milk is due to the formation of lactic acid from its lactose; this change is due to the growth of *BACILLUS ACIDI LACTICI*, which requires no air (anaërobic ferment) and thrives best between 35 and 40 degrees. (See plate).

9. The life process of ferments limits itself by AUTOTOXY, precisely as does the life process of true plants and animals. When 10 to 12 per cent. (by weight) of alcohol has been produced in the glucose solution, the cells cease growing; when 14 per cent. are present, the ferment is killed by its own product. The most favorable temperature for the growth of the ferment cells is between 28 and 34 degrees (the optimum). In concentrated glucose solutions (over 60 per cent.) the cells cannot live.

10. Pasteur has also proved that certain contagious and infectious DISEASES are fermentative; and that the system may be protected against the growth of these ferments or microbes by VACCINATION. The immunity enjoyed by our race against smallpox, since Jenner's day, can now be understood. The microbe is attenuated (weakened) by culture under unfavorable conditions; the liquid (serum) so produced may confer immunity to the system to which it is transferred (by inoculation, vaccination).

11. Medical research of the present is almost entirely dominated by the METHODS OF THE CHEMIST PASTEUR. Microbes, toxins, antitoxins, serums are the watchwords of the day and the chemist properly surrenders this new world to the physician and the biologist. But the new compounds produced—corresponding to alcohol in common fermentation—remain in the chemical laboratory.

12. Thus, many of these microbes produce alkaloidal compounds. If formed during life of the macro-organism, these compounds are called LEUCOMAINS (Gautier); if in the cadaver, they are called PTOMAINES, (Selmi). Several of

these latter simulate the solubilities and color reactions of the true vegetable alkaloids, strychnine, quinine, and others, and thus impose extra care on the part of the toxicologists. The former also show a like kinship; the leucomains xanthin and uric acid give the same murexid test as do theobromine and caffeine (theine). This may account for the general use of tea, coffee and chocolate.

## 72. PETROLEUM AND COAL.

1. Plants and animals have lived on this globe for ages; we find their unperishable remains in all stratified rocks (12). Such remains are called FOSSILS and casts, according as it is the original material (shell, coral, bone), or the same replaced by some other substance (silica).

2. Many limestone deposits are almost completely made up of shells and corals, due to the respiration of mollusks and polyps of the primeval sea. These enormous limestone deposits thus contain the carbon dioxide of the PRIMEVAL ATMOSPHERE, which must have been utterly irrespirable to warm blooded animals.

3. In such an atmosphere, vegetation must have been excessively luxuriant. The numerous coal deposits found in all parts of the globe confirm this conclusion by their extent and thickness; for COAL is the fixed residue of primeval vegetation, terrestrial and aquatic. Enclosed between two layers of rock, the vegetable material would mainly lose volatile constituents and become richer in carbon (carbonized).

4. Chemically we can distinguish only two kinds of coal, namely, BROWN-COAL and bituminous or BLACK-COAL, The first gives an acid distillate (acetic acid); when heated in a test tube, a moist blue litmus paper is reddened by the vapors. The second gives a strongly alkaline (ammoniacal) distillate. Anthracite seems to be the end-product of bituminous coal.

5. Mohr, the systematizer of volumetric Analysis (50, 1), found that wood and peat yield acid distillates, while dried sea weeds yield an alkaline distillate. He concluded that it is chemically impossible to derive bituminous coal from wood or peat; that this coal must have formed in the ocean from SEA WEEDS and still continues so to form to-day (Sargossa Sea of the Atlantic).

My own observations and analyses (48, 10) have confirmed the conclusions of Mohr. However, geologists continue to disregard the apparent chemical impossibility involved in their favorite theory of the origin of coal from trees of primeval forests and from peat bogs.

6. Chemically coal is a prime material of the utmost importance (12, 10). It forms the basis of most extended chemical industries. GAS WORKS yield tar, ammonia, cyanides and other products. The use of coal as fuel—and source of steam power—may be again replaced by water power, which, converted into electricity, may be widely distributed, as is being done at the present (Niagara).

7. AT BAKU, on the Caspian Sea, fire worshipers have maintained permanent fires from time immemorial. Over quite an extended region it is sufficient to dig or drill down a few feet into the ground to obtain a flow of gas that burns upon being lit. The Chinese have for centuries utilized such ho-tsings (fire-springs) in connection with their salt works.

8. Shortly before 1860, PETROLEUM was discovered in enormous quantities in Pennsylvania, and promptly refined for the market of the world as illuminating oil (KEROSENE). New wells were drilled, great fortunes were made, and oil fields sought for in other States. New York, Ohio, Canada and California have added to the production.

9. The example of America found imitators in the Baku region, which now is commercially highly developed. The oil is transported by a pipeline to the Black Sea, and shipped by tank-vessels. This last method has been adopted by the

American firms for export to Europe. The Rothschilds (with Nobel as engineer) control the RUSSIAN OIL; the Standard Oil Company (Rockefeller) controls the AMERICAN OIL. The two have divided the market of the world between them.

10. The total PRODUCT OF PETROLEUM is about fifty million barrels a year, of which America produces about 30, Russia about 20 million barrels. Galicia and Roumania produce half a million, Canada a quarter million barrels. Nobel has given millions of dollars to the University of Stockholm; Rockefeller has done the same for the University of Chicago. Thus petroleum will continue to give light.

11. THE CRUDE PETROLEUM is a limpid to thick liquid, not miscible with water. G 0.79 to 0.94. Wine colored to black. Etherial to offensive odor.

American petroleum is lighter colored and lighter weight, and gives about twice as much kerosene as the Russian; the latter leaves almost ten times as much of residue, non-volatile at 300°.

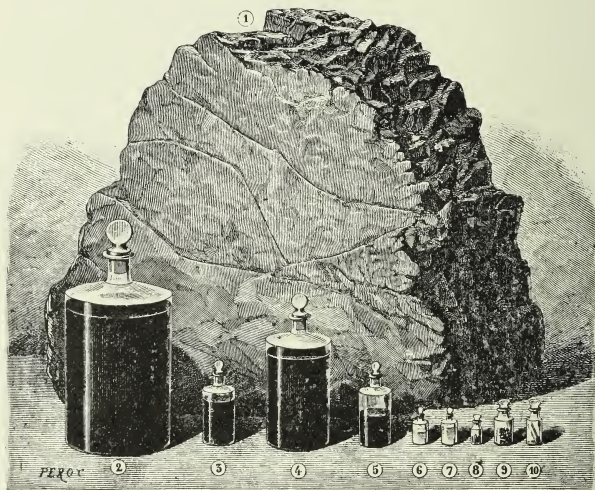
12. PETROLEUM IS REFINED by fractional distillation. The fraction passing over between 150 and 300° is kerosene, fit for illuminating purposes. It is further purified by washing with sulphuric acid, then with water, finally with dilute caustic soda; lastly re-distilled. American kerosene is nearly colorless, blueish fluorescent; G 0.79 — 0.80, flash-point above 21 degrees.

## 73. GAS AND TAR.

1. THE ILLUMINATION of the streets of cities is peculiar to modern times. The streets of Paris were the first illuminated (in 1667). Stationary oil lamps or lanterns were used, after attempts to make each householder keep a light burning all night in one window had failed.

2. When the handling of gases had become familiar towards the close of last century, it was natural to try to distribute by tubes the gas driven off by heat from combustibles for illuminating and heating purposes. Philip LEBON in France, Murdoch and Samuel CLEGG in England perfected plans and appliances. The inventions of the latter continue in use even to-day.

3. THE STREETS OF LONDON were illuminated by gas in 1812; those of Paris in 1815. Now even most small towns are illuminated by gas. IN ENGLAND, ten million tons of coal are used annually for making about three thousand million cubic meters of gas; four hundred million dollars capital being invested in the six hundred gas works of England.



Bloc de houille

représenté avec le volume proportionnel des principaux produits qu'on en retire.

1. Bloc de houille. — 2. Goudron. — 3. Huile légère. — 4. Huile lourde. — 5. Graisse verte ou huile à anthracène. — 6. Benzine. — 7. Toluène. — 8. Phénol. — 9. Naphthaline. — 10. Anthracène. (D'après les échantillons de la conférence de M. Wurtz.)



4. THE ILLUMINATING GAS produced represents only about 18 per cent. of the weight of the bituminous coal taken. About 70 per cent. remains as solid residue (coke) in the retort, while about 5 per cent. separates as tar and 7 per cent. as tar water in the condensers between the retort and gasometer.

5. The gas itself contains many NOXIOUS INGREDIENTS, especially sulphides and cyanides. These are removed by passing the gas over lime and basic iron sulphate. These materials become offensive when dumped; it has been necessary to work them up for sulphur and for cyanogen compounds. Thus noxious waste products have been made profitable.

6. THE COKE left in the retorts is larger in bulk than the coal used; it is a useful fuel, burning (like anthracite) without flame, but containing all the ashes of the coal used. THE TAR and TAR-WATER are run into pits where the two liquids separate. The most valuable constituent of the tar-water is ammonia; it is converted into sulphate, amounting to about one per cent. of the coal used.

7. THE COAL TAR PRODUCED in the gas works of the world amounts to over a million tons a year. Germany and the United States produce over one hundred thousand tons each, and England six hundred thousand tons a year. It is worked up mainly for coloring and disinfecting materials. The chemical coal tar industry is most highly developed in Germany.

8. The crude tar is first subjected to FRACTIONAL DISTILLATION. Four fractions are taken at about 170, 230, 270 degrees and above, called respectively light oil, middle oil, heavy oil and anthracene oil; the residual black pitch is drawn as viscid liquid from the boiler. Each of the four tar oils is subjected to further fractioning and chemical purifications.

9. In this way, the LIGHT OIL yields mainly benzol, toluol and naphta, together with a very small per cent. of

pyridine. The MIDDLE OIL furnishes mainly phenol and naphthalene. The HEAVY OIL gives naphthols, cresols and liquid paraffins. The ANTHRACENE OIL is the most valuable fraction, giving fast coloring materials (alizarin, 61.10); but its amount is small.

10. The purification and properties of the most important of these TAR PRODUCTS will be considered in another lesson. The graphical representation above given of the amount of these products, compared to the coal taken, is due to Wurtz (1876). The piece of coal (1) represented weighs about 300 grammes. Tar, 2. Tar Oils: light, 3; middle and heavy, 4; green, 5. Benzol, 6. Toluol, 7. Phenol, 8. Naphthalene, 9. Anthracene, 10.

11. QUANTITATIVE EXPERIMENTS on this dry distillation of coal are made by heating one to three decigrammes of coal in a glass tube, connected with a U-tube (submerged in water) and attached to a 100 cc. gas burette. The coke remains in the combustion tube, the tar and ammonia water are found in the U-tube, and 30 to 90 cc. gas collect in the burette. The illuminating gas weighs about half a milligramme per cubic centimeter. Air containing between 5 and 30 per cent. of the gas is explosive; most violently so when containing about 17 per cent.

12. By heating ten to twenty grammes of bituminous coal in a regular combustion tube, the tar and tar water will show up very nicely, and the gas may be collected in a glass-gasometer or burnt in a gas burner. The burners of the combination furnace nearest the U-tube should, of course, be lit first; the others are turned on gradually to maintain a steady flow of illuminating gas.

## 74. PHENOL AND ANILINE.

1. The pure chemical compounds, which, by means of repeated fractioning and washing with appropriate solvents are extracted from coal tar are often called AROMATIC COMPOUNDS. Of these, the most volatile BENZOL, has already been described (62.6). The others of general interest will now be considered. They are strongly acted upon by bromine and by nitric acid.

2. NAPHTALENE is extracted from the middle tar oil, from which it crystallizes upon cooling; it is purified by sublimation. When pure it, forms colorless lamellar crystals, retaining a peculiar, tar-like odor, and having a notable vapor tension even at 15°. F 79, B 218. Burns with very fuliginous flame. Insoluble in water, soluble in alcohol, ether and benzol. Moth balls and tar camphor are commercial forms of naphthalene.

3. ANTHRACENE is the most valuable constituent of the crude anthracene oil (green oil) coming over above 270°. By hot pressure the more fusible ingredients are removed. The solid residue is redistilled, the fraction passing over between 340 and 360 is retained, purified by solution in hot benzol and crystallization on cooling; finally it is sublimated. It forms colorless, rhomboidal tablets; F 210, B 350. Soluble in hot benzol, difficultly soluble in alcohol and ether, insoluble in water.

4. Benzol, naphthalene and anthracene are NEUTRAL SUBSTANCES, neither acid nor alkaline, insoluble in water. The tar oils contain a number of allied neutral bodies, differing in properties from the type compounds given. Thus TOLUOL (B 111, still liquid at - 28) remains liquid when benzol crystallizes; it has first been extracted from balsam of tolu.

5. PHENOL (carbolic or phenic acid) is extracted from the middle tar oil, after the naphthalene has crystallized out. The

residue is shaken with sulphuric acid to remove alkaline bodies. After this separation, the liquid is stirred with concentrated caustic soda and heated by steam, forming sodium phenate. From the separated pure solution, sulphuric acid precipitates crude carbolic acid, this being but slightly soluble in water. It is washed, dried over calcium chloride, and rectified. The liquid cooled to  $-10^{\circ}$  deposits crystals.

6. PURE PHENOL forms needle-shaped, colorless crystals. G 2.06; F 42; B 182.5. It has a burning taste, dissolves slowly in 20 parts of water, forming a solution not acting on litmus paper, nor decomposing alkaline carbonates. It is soluble in hot water, alcohol, ether, glycerin, fixed oils, fixed alkalies and ammonia; very caustic on skin (Ka bromide best antidote). It is strongly antiseptic. Ferric chloride colors it violet, even in dilute solution. Bromine water gives a white precipitate.

7. Associated with phenol are the CRESOLS, which are more liquid (F 6 to over 40 below) and less volatile (B from 5 to 15 higher) than phenol. They are more strongly antiseptic than phenol, and thus make crude phenol much more antiseptic than pure phenol; but also much more poisonous. The most liquid cresol is the strongest in this regard; it is especially abundant in the tar from pine and beech wood.

8. The heavy tar oil contains two closely related substances distinguished as ALPHA ( $\alpha$ ) and BETA ( $\beta$ ) NAPHTOL. Both are soluble in hot water, alcohol, ether, and benzol; both are crystallized solids, and smell faintly like phenol. They are distinguished by the following characters.  $\alpha$ -Naphthol, most poisonous, silky needles, F 94, B 278, violet with ferric chloride;  $\beta$ -Naphthol, not so poisonous (used externally), pearly scales, F 123, B 285, greenish with ferric chloride.

9. The heavy tar oils contain also minute amounts of three remarkable alkaline bodies, pyridine, chinoline and aniline. They are taken up by the sulphuric acid used in the process of purifying the more abundant substances described. By

super saturation of these acids with lime and distilling, the TAR BASES are obtained. They occur in much larger amount in bone oil, from which they are therefore more generally obtained.

10. PYRIDINE is a colorless liquid with penetrating, characteristic odor, miscible with water; G 0.99 at 0°, B 115.

When an alcoholic solution of pyridine is treated with a fragment of metallic sodium, the liquid assumes the odor of pepper, and contains the new alkaline liquid called PIPERIDINE (B 106) forming crystallizable salts with acids.

11. CHINOLINE is a colorless, strongly refracting liquid of specific, penetrant odor. G 1.095 at 20°, B 239. It forms crystallizable and soluble salts with acids; its bichromate is difficultly soluble, and forms as precipitate in sufficiently concentrated solutions. Distilling cinchona bark (or its alkaloid) quinine with caustic potassa yields a distillate containing chinoline; hence its name.

12. ANILINE is a colorless, oily liquid, turning yellow and finally dark brown on exposure to the air. Its odor is weak, but peculiar and unpleasant. G 1.031, B 149, solidified at -8. Very soluble in water and in alcohol; precipitates many metals (Zn, Fe, Al) from their aqueous solutions. Chloride of lime colors its aqueous solution violet purple. Chromic acid colors it first red, then violet and finally blue in the presence of strong sulphuric acid. Potassium bichromate gives a dark green color, burning black. Aniline was first (1826) obtained in the dry distillation of indigo (called ANIL in Spanish.) It is the basis of aniline colors.

## 75. BONE OIL AND WOOD SPIRITS.

1. Exposing an organic compound in a retort to a bright red or beginning white heat, while preventing the air from access to the same, drives off all that is volatile. The vapors liquefy in cooled vessels (condensers) and the gases are col-

lected in gasometers. Such a process is called DRY DISTILLATION. The products obtained are four in kind: solid coke, liquid tar and tar water, and the gas mixture. Lecture 73.

2. Evidently the same material will give DIFFERENT PRODUCTS not only according to the degree of heat used, but even according to the size of the retort and the readiness wherewith the products can escape from the same. The higher the temperature, the further the destruction (decomposition) by heat will be carried. In a narrow retort with narrow escape opening, the products will be exposed longer to the decomposing effects of the heat of the retort.

3. These influences are well understood in the great industry of illuminating gas. To obtain RICH ILLUMINATING GAS, the decomposition must not be carried too far. High temperature, a beginning white heat ( $1200$  to  $1400^{\circ}$ ), and large openings for the escape of the gaseous products give the best illuminating gas. Lower heat gives better tar. In merely coking the coal for iron furnaces, the coke must be compact; hence the coal is piled high enough to exert pressure.

4. This process is also very appropriately called DESTRUCTIVE DISTILLATION. All vegetable and animal substances give the four kinds of products, varying in proportion. Thus animal materials give strongly ammonical tar water, while wood gives acid tar water. To this extent destructive distillation furnishes information concerning the chemical composition of the substance used.

5. Each of the four products obtained is again VERY COMPLEX, as has been sufficiently shown in the study of the dry distillation of coal. The composition of the gas, and especially that of the tar, is extraordinarily complex, for a great many chemical substances can be extracted therefrom by appropriate methods.

6. We cannot give detailed attention to this interesting and difficult analytical process. But in presenting an outline of the dry distillation of WOOD, BONES and SHALES we not

only shall obtain important compounds from these prime materials, but also throw considerable light on the question raised. The products obtained strikingly represent the material used.

7. BONES are subjected to dry distillation in the manufacture of Boneblack or animal charcoal (69, 11). The famous Dippel's Oil is rich in the alkaline bodies pyridine and chinoline (74, 9-11) to which it mainly owes its medicinal effects. The animal oils of earlier chemists—such as the OIL OF VIPERS, distilled from live vipers—contained the same bases. (Lemery, edition Baron, pp. 669-674; Paris 1757).

8. WOOD yields upon dry distillation a strongly acid distillate. Much of the acetic acid of the market is obtained by this process. The highest amount of acid is obtained at low temperature, not exceeding  $400^{\circ}$ . The charcoal left in this case is brownish, its temperature of ignition is correspondingly low. Beech wood yields, per hundred, about 25 charcoal, 5 tar, 45 crude wood vinegar and 25 of gas. The tar from beech wood is specially rich in CREOSOT, the meat preservative of smoke. Creosot concentrated and purified is called guajacol (G 1.12, B 201). Bituminous SHALES give largely paraffins and the so called solar-oil.

9. THE PRINCIPAL CONSTITUENTS of the tar water from wood are pyroligneous or acetic acid (B 118), wood spirits (B 66) and aceton (B 56). Saturating with milk of lime precipitates the acid as calcium acetate, from which the liquid is distilled off. Redistilling with chloride of lime converts the acetone into chloroform (B 61), which passes over first; the almost pure wood spirits (methyl alcohol) is collected above  $66^{\circ}$ .

10. Distilling the CALCIUM ACETATE with concentrated muriatic acid gives ACETIC ACID, which is purified by distillation with potassium bichromate in silver retorts. The use of sulphuric instead of muriatic acid is objectionable, since gypsum precipitates, and organic substances present reduce the sulphuric to sulphurous acid, which distills over with the acetic acid from which it is difficultly removed.

11. ACETIC ACID, in its most concentrated form (glacial), solidifies at 17; B 118. G 1.08 at 0°. It has a characteristic, suffocating odor, and a strong acid taste; it is very corrosive. It dissolves many metals, forms salts (acetates) which are almost all soluble. It is the oldest acid known.

Forming by oxidation of alcohol, its lead and copper salts were made in antiquity by covering the metals with the residue drawn from the wine press. 71, 8.

12. METHYL ALCOHOL is a colorless, limpid liquid of a pleasant ethereal odor. G 0.81, F - 134, B 66.5. Miscible with water, alcohol and ether, and as solvent generally as effective as alcohol.

ACETONE is a colorless liquid of ethereal odor, G 0.81, B 56, soluble in water, alcohol and ether. With sodium bisulphite it forms a crystalline compound.

CHLOROFORM is a colorless liquid of pleasant, characteristic odor, hardly soluble in water, miscible with alcohol and ether, G 1.48, F - 70, B 61. We shall soon study these substances more in detail.

## 76. STARCH, SUGAR AND GLUCOSE.

1. The principal prime materials of the organic world have now been considered. It has also been shown how DEFINITE CHEMICAL COMPOUNDS have been extracted from these—many thereof having been in use since antiquity. It will next be necessary to consider some of the CHEMICAL CHANGES of these leading organic compounds.

2. The sweet principle of the cane (sucrose) and of the grape (glucose) we considered in the first lesson (58) of our organic chemistry; the most important cellular substance, starch, was considered later on (66). We shall now show how both starch and sucrose are readily CONVERTED INTO GLUCOSE by simple chemical means.



3. Starch, thoroughly wet by rubbing with a little water, then boiled with much water, gives starch paste (66, 10); when cold, this gives the delicate iodine reaction (blue). But if a little dilute sulphuric acid be added to the boiling starch paste, this will gradually get thin. If the boiling is stopped while the liquid still is sticky, it gives a precipitate with alcohol, but no blue with iodine. The starch has been converted into DEXTRINE.

4. If the boiling continues, the starch solution will finally cease to be sticky, and give no longer a precipitate with alcohol. If the acid is now neutralized (say by adding a slight excess of powdered chalk), the solution will give the glucose reaction (58, 6). Accordingly the STARCH HAS BEEN CONVERTED INTO GLUCOSE. Dilute muriatic acid (1 per cent.) effects the conversion more completely.

5. The roots of most compositæ (*Inula helenium*, *Dahlia*, *Helianthus*, *Taraxacum*, etc.) contain a pseudo-crystalline substance, soluble in water, precipitable by alcohol, tinted yellow by iodine, called INULIN, and considered to take the place of starch. It rather seems to correspond to amidine (66.10) and may, therefore, be called levulin; for boiled with dilute acids it yields a glucose, deporting itself chemically exactly as the glucose made from true starch.

6. Physically the glucose from starch and from inulin act in almost opposite manner on polarized light. The solution filled into a brass tube (10 or 20 cm. long), closed with plane plate glass at the ends, turns the plane of polarization of light to the RIGHT in the case of glucose from starch, to the LEFT in case of glucose from inulin. These two forms of glucose, accordingly, are called DEXTROSE and LEVULOSE.

7. HONEY contains both kinds of glucose, namely, dextrose and levulose. By stirring up honey in cold alcohol, only the levulose is dissolved; the dextrose is separated by filtration and pressure, and can be dissolved in boiling alcohol, from which it will crystallize upon cooling.

8. Sucrose dissolved in water, very slowly changes into a mixture of levulose and dextrose, called INVERT-SUGAR. By heating, the process is accelerated. It is quite prompt when sucrose is boiled with dilute acid; the boiled solution, after neutralization, will exhibit the glucose reaction with Fehling's solution. Sugar boiled with fruit (acid juice) is also inverted; hence in putting up fruit, sucrose ought to be added last.

9. Sucrose solutions do not ferment; syrups keep quite well. But all forms of GLUCOSE FERMENT promptly. Hence starch sugar is made on a commercial scale (from potato starch in Germany, from corn starch in the United States) and some finds its way to breweries, acetic acid works, and even to other factories.

10. Claude Bernard (p. 36) discovered (1856) animal starch (GLYCOGEN) in the liver, and in oysters. The latter may be crushed in a mortar, and thrown into boiling water; if to the cold, opaline filtrate, a large amount of alcohol (or glacial acetic acid) is added, the glucogen separates as a white, amorphous powder. It is changed into glucose (dextrose) exactly as is starch.

11. All farinaceous food consists largely of starch, which can only enter the blood in soluble form, as glucose. The liver evidently takes a prominent part in effecting this change. In a normal state (health) this glucose is used in the system (assimilated). In DIABETES MELLITUS, large amounts of glucose are drained from the system in the kidneys. The urine becomes exceedingly abundant in volume, high in specific gravity (1.035) and gives the glucose reaction with Fehling's solution.

12. Cellulose, by protracted boiling with dilute acids, can also be converted into glucose (SUGAR OF RAGS); more rapidly if the acid is stronger, when much material is lost by charring. Fusing cellulose with caustic potash, or boiling sugar, glucose or starch with rather strong nitric acid, yields OXALIC ACID (63, 10) as the common oxidation product. From the nitric acid it separates on cooling in crystal form.

NOTES.—GUM ARABIC is an exudation from species of acacia and mimosa in northern Africa and the Orient. It is colorless, soluble in water, insoluble in alcohol, like dextrine, which latter is accordingly often called British Gum. In that case dextrine has commonly been manufactured by moistening a ton of starch with 300 kgr. of water, to which 2 kgr. of common nitric acid had been added. The mass, after being air dried, is heated, in thin layers, to 100 ; in about an hour or two it has changed to dextrine.

Gum Arabic solution, boiled with dilute acid, yields a glucose (arabinose), precisely as does dextrine.

MUCILAGE is extracted by boiling water from linseeds and other materials. Mucilages resemble gums.

PECTINE dissolves in hot water and gelatinizes on cooling. It is precipitated by absolute alcohol from certain fruit juices (black currants, etc.), after having removed lime by oxalic acid and albuminoid substances by tannin.

## 77. ALCOHOL AND ETHERS.

1. The extraction of alcohol from wines has been shown (58, 11), and its industrial production mentioned (58, 12). We have also seen how dilute alcohol is converted into an acid (71, 8) and how this acetic acid is industrially obtained (75, 11) in concentrated form. Dilute acetic acid, obtained from alcoholic liquids, is called VINEGAR, and is used in the preparation of food and at table; it retains the flavor of its origin.

2. If to a little water in a test tube is added at least an equal volume of concentrated sulphuric acid, the mixture will be quite hot. If now a few drops of alcohol be added, the pleasant odor of ETHER will be noticed. If a crystal of any acetate be dropped into this liquid, the more fragrant odor of ACETIC ETHER will be recognized. Compare 55.12. Such effects have already been observed by the alchemists; Lully in the 13th, Valentin in the 15th century.

3. This simple test shows how common and compound ethers are obtained, namely by distilling alcohol with much

sulphuric acid alone and with some organic or other acid. The ether, being very volatile **QUITE INFLAMMABLE**, and forming explosive mixtures with air, this distillation must be made with great care, and by experienced operators only. In ether factories, all heating is done by steam carried from another building, so that no fire nor flame is allowed in the building where ethers are made.

4. To obtain **COMMON ETHER** (so-called sulphuric ether) 200 gr. of sulphuric acid are mixed with 120 gr. alcohol, and the mixture distilled at 140 to 145 degrees. By a special contrivance, a continuous, though small flow of alcohol, corresponding to the ether distilled over, may be kept up till the acid becomes inert when too dilute from water formed in the process. The receiver must be well cooled.—The ether formed contains no sulphuric acid.

5. The **CRUDE ETHER** so obtained is treated with milk of lime for a day, and frequently agitated therewith; this removes the acid that has passed over. The ether is next washed with water, dried on calcium chloride, and finally rectified over metallic sodium on the water bath, if the last traces of water and alcohol are to be removed.

6. **PURE ETHER** is a very limpid, colorless liquid of a strong, characteristic and pleasant odor, and a sharp, burning taste. G 0.75 at 0, B 34.5; it solidifies to crystalline scales at  $-31^{\circ}$ . It is non-miscible with water, on which it floats. It mixes with alcohol in all proportions. Water dissolves, upon shaking, about one-tenth its own volume of ether. Ether is a most important solvent (S, P, I) especially for fats and oils. Very combustible and inflammable, see above (3).

7. By distilling a mixture of (fused) sodium acetate, alcohol and sulphuric acid in the proportions of 10, 6, 15, crude **ACETIC ETHER** is obtained. It is purified by shaking with milk of lime and rectification from calcium chloride. G 0.91 at 0, B 74; water dissolves one-seventh its own volume; mixes with alcohol in any proportion. It is a solvent of resins and

gun cotton. Wine and wine vinegar contain a sufficient amount of this ether to be recognized by the very characteristic odor.

8. When acetic ether is treated with sodium hydrate, alcohol reappears, and can be distilled off; the solid residue is sodium acetate. Thus the original substances are reproduced; the REACTION HAS BEEN REVERSED. Consequently alcohol must be a hydrate of some radical, passing into the ether by mere double decomposition. Liebig (p. 23) called this radical ETHYL, symbol Et.

9. The reactions involved are all DOUBLE DECOMPOSITIONS. In the formation, Na Ac<sup>ate</sup> and Et H<sup>ate</sup> (alcohol) give the volatile Et Ac<sup>ate</sup> (acetic ether) and Na H<sup>ate</sup> in presence of excess of heated strong sulphuric acid, which forms Na S<sup>ate</sup> and absorbs H H<sup>ate</sup> (water). When the acetic ether is treated with Na H<sup>ate</sup> at common temperatures, alcohol (Et H<sup>ate</sup>) and Na Ac<sup>ate</sup> reform; the first can be distilled off, the latter remains as salt.

The formation of common ether now is readily understood. Alcohol, as ethyl hydrate, Et OH, in contact with the hot, concentrated, hygroscopic sulphuric acid, gives off water and becomes ether or ethyl oxide, Et<sub>2</sub> O. Two alcohol give one each of water and ether, namely 2 Et OH give H<sub>2</sub> O and Et<sub>2</sub> O.

10. Many other ethers are distilled in a like manner from alcohol and the salt in presence of an excess of strong sulphuric acid. Thus common salt (Na Cl<sup>ide</sup>) yields CHLORIC ETHER. Heating chloric ether with water in a covered vessel under moderate pressure gives alcohol and muriatic acid. This double decomposition again shows that alcohol is ethyl hydrate.

11. When, however, strong muriatic acid (H Cl<sup>ide</sup>) and alcohol (Et H<sup>ate</sup>) are heated in an AUTOCLAVE (28, 3-4) up to 140°, or under a pressure of 40 atmospheres, chloric ether (Et Cl<sup>ide</sup>) and water (H H<sup>ate</sup>) are formed by double decom-

position. This reversible reaction again confirms the constitution of alcohol as ethyl hydrate. Under 40 atmospheres the reaction is the reverse of that under one or two atmospheres. The ether  $\text{Et Cl}^\text{ide}$ , boils at 11 degrees. It is sold in strong, sealed glass tubes and used as a local anesthetic.

12. Taking potassium nitrite—and better strong muriatic, instead of sulphuric acid—NITROUS ETHER is obtained, which as 5% solution in alcohol is a valuable remedy, called sweet spirits of nitre. Also this reaction is reversed; for potassium hydrate added to the nitrous ether gives again potassium nitrite and alcohol. Thus the ethyl radical forms alcohol with  $\text{H}^\text{ate}$ , and ethers with acid radicals. Nitrous ether boils at  $17^\circ$ .

## 78. FATS AND SOAPS.

1. Oil and water do not mix. By shaking, temporary emulsion may be obtained, which soon separates again in the two layers of water and oil. But if an alkali is dissolved in the water, and the mixture gently heated, complete solution is effected; a SOAP is produced. This solution of a fat in an alkaline aqueous liquid is called SAPONIFICATION.

2. Wood ashes used instead of caustic alkali effect an incomplete solution only. The Gauls, according to Pliny, operated in this manner. In modern times the cheapening of the process has made soap available to everybody. England produced in 1791 twenty thousand tons of soap, worth eight million dollars; ninety years later, it produced eight times as much, costing only a little more than twice as much (eighteen million dollars). Industrial progress had brought the price down to one-fourth.

3. Alkalies are not the only substances that make oil dissolve in water on moderate heating. Litharge has a corres-

ponding effect; the product, called PLASTER, differs from ordinary soaps. The great chemist, Scheele (p. 169), repeating this process in his little pharmacy in Sweden, discovered 1779 the "sweet principle of oils," which we now call GLYCERIN, in the aqueous liquid remaining when the plaster is finished.

4. Chevreul (p. 37) completed the PROXIMATE CHEMICAL ANALYSIS OF THE FATS as early as 1815, mainly by a chemical examination of the old process of saponification. He first separated the natural fats into simple fats (59.9) such as olein, stearin. He next found that each simple fat, in saponification, really undergoes a double decomposition with the caustic alkali (hydrate). Consequently, FATS ARE SALTS (OR ETHERS). Glycerin is the common base of all fats.

5. Thus, stearin is glyceryl stearate, if the radical of glycerin be denoted according to Liebig's system (yl). With caustic potassa (potassium hydrate) on boiling, double decomposition takes place. Soap is formed, that is potassium stearate (soft soap). Glycerin, accordingly, must be GLYCERYL HYDRATE. If salt is thrown into this soap solution, sodium stearate (hard soap) separates, being much less soluble than soft soap.

6. Chevreul dissolved four parts of fat in two parts of water containing one part of caustic potassa. The solution was effected on the water bath. When complete, he dilutes with water and adds just enough tartaric acid to neutralize the potassa; THE FATTY ACID, being insoluble in water, separates on cooling, forming an oily layer or a solid cake. By washing with water this acid is purified.

7. THE REACTION involved is again merely a double decomposition. Soap from stearine by caustic potassa is potassium stearate. Adding to its aqueous solution hydrogen tartrate gives potassium tartrate (difficultly soluble) and hydrogen stearate or stearic acid, insoluble in water. On the hot solution this acid forms an oily layer, which solidifies to

a fatty cake on cooling. Palmitic acid appears in the same form. Oleic and butyric acids are liquid at common temperatures. The last is volatile and can be distilled off.

8. THESE FATTY ACIDS are soluble in alcohol and ether, from which they crystallize below their melting point. This is, for stearic acid 69, palmitic acid 62, oleic acid 14. Butyric acid solidifies below the freezing point and boils at 163. The other fatty acids named, when heated, decompose before boiling. With steam they volatilize, like many volatile oils (60, 3). The so-called stearin candles consist mainly of stearic acid and not of stearin.

9. It is evident that a mixture of fatty acids can be more readily separated than the corresponding mixture of the fats. Accordingly, saponification is generally resorted to in THE ANALYSIS OF FATS. Butyric acid is distilled off. Oleic acid decanted and pressed from the solids. The amount of potassa (in mgr. per gramme of fat) required for saponification (Koettstorfer's number) is determined by difference. The amount distilled off is determined by tenth-normal alkali; the number of cc required for 5 grammes of fat is called Reichert's number. It is most important in testing butter.

10. The soap and stearine candle industries have flourished especially in France, where the principal chemical investigations of the fats have been made. The soap industry at Marseilles is the most extended and oldest in the world; it is the commercial center of the olive oil region. Genuine castile soap is made from this oil. France excels also in toilet soaps, on account of the perfumes required (60, 5-7).

11. The DIRECT DECOMPOSITION OF FATS into acid and glycerine is effected by high pressure steam (10 atmospheres). After several hours' action, the glycerin is dissolved in the water while the fatty acids, floating on the surface, are blown over with the steam. The glycerin so obtained is the purest in the market. This process is largely employed in England and in the United States.



12. The direct SYNTHESIS OF FATS from their constituents, acid and glycerin, has been effected (in 1854) by Berthelot (p. 27). It takes place at common temperatures to a very slight extent in a very long time. It is quite slow even at 100 degrees. In the autoclave, at 200 degrees (or about 16 atmospheres) Berthelot effected the synthesis in a few hours, in three distinct stages, (proving that glycerin is a tri-valent base 43, 11). Here we have witnessed another most remarkable reversible reaction.

## 79. NITROGLYCERIN AND GUN-COTTON.

1. Man alone has not been endowed with special ORGANS OF DEFENSE, nor is he swift enough to escape. But intelligence has armed his hand, and courage needs no wings to flee. Thus primitive man conquered the animal world in the golden age, with stone and bow, with ax and spear.

2. In his contests for dominion, man depended for ages on the strength of his own MUSCLE. The armies of the Romans, and of the Saracen and Christian Knights during the Crusades, exhibit this phase of man in its highest form. When cunning and over-confidence decide the contest, as at Troy, we feel sympathy neither for the victor nor for the vanquished.

3. About equally remote in time, the contest between David and Goliath foreshadows the contrast between modern and ancient arms. Reading the dramatic account in the Scriptures (1 Samuel 17) one is fascinated by the parallel. Goliath, proud of his muscle; David, frail youth, conquers by MECHANICAL SKILL, long before the arm of the giant can reach him.

4. THE EXPLOSIVES, furnished by chemistry, have endowed the modern soldier with a power incomparably greater than his own muscular strength. The introduction of the crude black powder changed the condition of man; serfdom was doomed when the blunderbuss took the place of the spear.

During the half century now closing, CHEMISTRY HAS AGAIN GREATLY ENLARGED THE RANGE AND POWER OF THE INDIVIDUAL; we may hope it will lift the burden of militarism from the race.

5. In BLACK POWDER or gun-powder, we have a MIXTURE of two combustible substances (C and S) with a sufficiency of nitre to furnish the oxygen to completely burn them (21, 12). A spark is sufficient to start the combustion. This suddenly converts the small amount of solid powder into a very large volume of hot gas. The pressure thus produced is about two thousand atmospheres. The projectile is thrown, or the rock is broken by the force of such an explosion.

6. The modern chemical explosives (nitroglycerin, gun-cotton, smokeless powder) are not explosive mixtures, but essentially EXPLOSIVE COMPOUNDS. The combustible materials (C, H) are in atomic proximity to the oxygen of the compound. The action is therefore instantaneous, so much so that the air acts like a resistant solid. A drop of nitroglycerin, exploding on a hard steel plate, knocks a hole into the same—the air acting like the sand tamping in a blast hole charged with black powder.

7. The work of the last fifty years has therefore been mainly directed to find means to TEMPER THE VIOLENCE of these modern explosives. Schoenbein, in Germany, discovered gun-cotton (1846), Sobrero, of Turin (1847) nitroglycerin. Nobel, of Sweden, tempered the later in dynamite (1867), which ever since has done man's work in mine, quarry and tunnel. Turpin and Vieille, of France, in 1888 made the first practical smokeless powder. The three steps taken are about twenty years apart in time.

8. NITROGLYCERIN is made by pouring glycerin into a cold mixture of concentrated nitric (3) and sulphuric acid (5 parts per unit of glycerin). The nitroglycerin (G 1.60), floating on the cooled, acid mixture, is separated and washed with water and soda solution. It is sweetish. Being extremely explosive,

it is not accepted for transportation in most countries. By a blow or concussion it explodes instantaneously; small amounts burn quietly in an open vessel. Its products of combustion are carbon dioxide, water, nitrogen and a slight excess of oxygen.

9. Nitroglycerin is an ether, corresponding to the original fat itself; namely GLYCERYL NITRATE. For when treated with caustic potassa it yields, by double decomposition, potassium nitrate and glyceryl hydrate or glycerin. The sulphuric acid simply takes up the water in the process. Nitroglycerin is absorbed by infusorial earth in the proportion of three to one. The mixture called DYNAMITE, feels dry, is reasonably safe, accepted for transportation under proper restrictions, and has for a quarter of a century been the most effective industrial explosive.

10. Cotton soaked in the same acid mixture is converted into GUN-COTTON. If the mixture is less concentrated, PYROXYLIN results. The first contains about 14 per cent. of nitrogen, the latter only 11. A solution of ferrous sulphate in concentrated muriatic acid decomposes either with evolution of nitric oxide gas; the volume of which, determined by the gas burette, gives the per cent. of nitrogen introduced. Pyroxylin is soluble in a mixture of alcohol and ether; the solution, on spontaneous evaporation, leaves a film of collodion. Gun-cotton is not soluble.

11. While not soluble in any solvent, true gun-cotton gelatinizes with acetic ether and with acetone, especially upon the addition of a little camphor. SMOKELESS POWDER is mainly such gelatinized gun-cotton and pyroxylin, of about 13 per cent. nitrogen. It is rolled into plates, cut into small squares, which are lightly covered with graphite. Giving no solid product, its explosion gives no smoke, only a light cloud of watery vapor.

12. To explode either black or smokeless powder, MERCURIC FULMINATE caps are used. It is made by adding

alcohol to a solution of mercuric nitrate. The process is very dangerous, therefore the particulars need not be given.

With cannon hurling a ton weight ten miles, rapid firing guns able to kill a hundred men a minute, and torpedoes that will blow up a five-million-dollar iron clad in an instant, we may hope that attack will soon be useless.

## 80. CHLORACETIC ACID AND CHLORAL.

1. In the four preceding lessons a number of chemical changes of organic compounds have been presented. In no case have we noticed any chemical reaction other than those common to inorganic chemistry (see Lecture 28). Thus far, most processes involved a DOUBLE DECOMPOSITION. It will be advisable to select also a few striking instances of substitution.

2. As far back as 1815, Gay-Lussac noticed that wax, bleached with chlorine gas, absorbed some thereof without change of volume in the gas. Faraday, in 1824, and Liebig and Bunsen, in 1832 discovered similar cases of SUBSTITUTION OF CHLORINE FOR HYDROGEN in organic compounds. Soon after (1834) Dumas made this a subject of transcendent chemical importance.

3. In 1840, Dumas changed acetic acid into TRI-CHLORACETIC ACID by simple substitution. Large, dry, glass stoppered flasks were filled with dry chlorine gas. A small amount of glacial acetic acid was introduced into each; only 9 decigrammes per liter. Exposed to bright sunshine, the walls of these flasks soon were covered with small, colorless, crystals of (tri-)chloracetic acid.

4. In this process there is NO CHANGE IN VOLUME of the gas, neither increase nor diminution. Accordingly, hydrogen and chlorine replace one another in equal measures, or

equivalent for equivalent. Therefore MH, the organic compound, and Cl Cl, the gas (40, 10) give M Cl and H Cl, the latter equal in volume to the chlorine gas taken. In a certain sense, this substitution may be considered a double decomposition.

5. Finally, quantitative determinations show that every equivalent of acetic acid (60 mgr.) has taken up three equivalents of chlorine gas (36 cc). Hence the substituted acid is called TRI-chloracetic acid. It crystallizes in rhombohedræ, rather deliquescent. G 1.42, F 46, B 195. Forms salts isomorphous with the corresponding acetates.

6. A given weight of purified crystals of chloracetic acid, when saturated by normal potassium hydrate, shows the equivalent to be 163.5. This furnishes the simplest demonstration that it is tri-chloracetic acid. For the SATURATING EQUIVALENT of acetic acid is 60. Substituting three chlorine (106.5) for 3 hydrogen (3) will increase the weight of the equivalent 103.5, making it 163.5, as easily confirmed by experiment.

7. The solution of potassium chloracetate, gently heated with an excess of potassium hydrate, yields CHLOROFORM (75, 12), readily recognized by its odor. This shows that the essential part of chloroform is a constituent of trichloracetic acid. When sodium amalgam is added to the acid or to its salts, the nascent hydrogen produced reduces the acid to the initial state, acetic acid.

8. The production, by Dumas, of this remarkable acid, exerted a most decisive influence on the development of organic chemistry during the last half century. The general law of ORGANIC SUBSTITUTION was now admitted to be, EQUIVALENT FOR EQUIVALENT.

9. When absolute alcohol is saturated at the freezing point with chlorine gas, ALDEHYDE is formed. The name was coined by Liebig on the American OMNIBUS principle, to indi-

cate that the new substance is ALcohol DEHYDrogenatus. The same product is obtained by a moderated oxidation of common alcohol, say with potassium bichromate and sulphuric acid. The purified aldehyde is a limpid liquid, of suffocating odor, G 0.80, B 21, soluble in water, alcohol and ether. It reduces silver from ammoniated silver nitrate on gently warming the solution (mirror).

10. If absolute alcohol is fully saturated with dry chlorine gas—the temperature being properly regulated—CHLORAL is formed. It is purified by distillation, first from sulphuric acid, thereafter from quicklime. It is a colorless, oily liquid. G 1.54, F  $-75$  (solidifies), B 98. Soluble in water and alcohol. When treated with nascent hydrogen (from zinc and sulphuric acid) it is reduced to aldehyde. Chloral reduces silver solution like aldehyde. Both form a crystalline precipitate with sodium bisulphite.

11. With water, chloral combines to CHLORAL HYDRATE which forms fine colorless crystals. F 46, B 97. Hence chloral is generally employed as hydrate. It is a most valuable hypnotic. When treated with potassium hydrate, chloroform is produced. Since blood is alkaline, chloral probably is gradually converted into chloroform in the system (Liebreich). Heated with nitric acid, chloral and its hydrate, yield trichloroacetic acid, which is most readily produced by this method.

12. The reactions given prove conclusively that alcohol, aldehyde, chloral, trichloroacetic acid and acetic acid are VERY CLOSELY RELATED mutually and to chloroform; for we have transformed most of these bodies into one or more of the others, and obtained chloroform from several of them. To enter more fully into the mechanism of these changes, we must now begin the study of their chemical composition.

## 81. PROXIMATE AND ULTIMATE ANALYSIS.

1. The materials furnished by nature we have found to be essentially COMPLEX. The rocks are all complex, most minerals contain admixtures of others—to us, impurities—and only in the finest, crystallized specimens do we find a true chemical individual, a single chemical compound. Organic materials are every way more complex than even the rocks.

2. To determine the real CHEMICAL COMPOUND ACTUALLY PRESENT in a given mineral or rock is often quite difficult, and not unfrequently impossible. We can always ascertain what elements are present, but in many cases it is impossible to state how they are combined, or what proximate compounds are contained in the sample. Thus it is even impossible to state exactly what salts are contained in a given mineral water, though it is conventionally done with a sublime disregard of knowledge.

3. To determine the proximate CONSTITUENTS OF ORGANIC MATERIALS is not less difficult. The substances themselves, being so readily changed by even contact with neutral solvents, greatly adds to the difficulties. However, by care and skill, the principal classes of organic compounds can be separated. The methods used for this purpose have been exemplified in the preceding lectures.

4. Chemists have endeavored to bring this work into a system. Thus Dragendorff has suggested an order of procedure for PLANT ANALYSIS. Ether removes fats, and alcohol resins, without changing starch, gum and proteid substances; hence they conveniently precede water and aqueous solvents. But no one system is applicable in all cases.

5. A careful review of the METHODS ACTUALLY EMPLOYED in our preceding lectures will be more beneficial than a lengthy exposition of any special system of procedure.

We will merely add that these extractions either have for their object the determination of the amount of a certain constituent or the preparation thereof for further research. In the first case, the substance used is limited, and must be most completely exhausted by freely using reagents and time; in the latter case, both the material and the reagents are used freely, to secure the purest product obtainable.

6. Such methods give us knowledge of the proximate constituents of organic substances. They are methods of PROXIMATE ANALYSIS. Thus we determine the amount of nicotine in tobacco, the percentage of morphine in opium, of sucrose in the cane, of glucose in the grape, of starch in the grain, of albumen in the egg. The results should not be stated with a precision that is fictitious. Chemists should not pretend to have done what is impossible. The thousandth of a per cent. is sheer humbug.

7. When an organic compound has been produced in the pure state, it may be subjected to ULTIMATE OR ELEMENTARY ANALYSIS as the first step in the search of its chemical composition and structure, expressible by appropriate chemical formulæ. It is evidently an utter waste of time to attempt the establishment of a chemical formula for anything not itself a true chemical compound.

8. Lavoisier showed that the four elements C, H, N, O constitute the bulk of all organic materials; they have even been termed ORGANOGENS. In a very large number of compounds, nitrogen does not occur; they consist of C, H, O only. On these facts the common method of ULTIMATE ANALYSIS BY COMBUSTION was planned by Lavoisier, improved by Gay-Lussac, and practically perfected by Liebig.

9. The organic compound—pure and dry—is mixed with a large excess of purest copper oxide (Gay-Lussac). The mixture, heated in a combustion tube, produces  $H_2O$  from H,  $CO_2$  from C, and N as gas, the organic substance burning at the expense of the oxygen of the copper oxide. The water and carbon dioxide produced are collected and weighed as



shown previously (32, 6); the volume of nitrogen gas produced is measured. The important PRACTICAL DETAILS of such combustion must be studied in the laboratory.

For educational purposes and elementary LABORATORY PRACTICE, small and short combustion tubes can be used over four wing gas burners in a row, the tube protected with a sheet of brass or iron. If no N, only the U-tube and gas burette with air lock for  $\text{CO}_2$  is required; if N present, insert potassa bulb and use gas burette for N.

10. The total amount of CARBON in the organic substance taken is  $\frac{3}{11}$  of the increase of the potassa bulb ( $\text{CO}_2$ ); the amount of HYDROGEN is  $\frac{1}{9}$  of the increase of the U-tube ( $\text{H}_2\text{O}$ ); compare 31, 7 and 5. The weight of the NITROGEN is  $1\frac{1}{8}$  mgr. per cc under common conditions (49, 8). The OXYGEN in the compound cannot be determined directly (55, 12; 53, 12); it is determined by difference.

11. Dividing the weights so obtained for C, H, N (and O) by the weight of the substance used, gives the amount of each element PER UNIT OF WEIGHT. Moving the decimal point two places to the right, gives the PERCENTAGE of each. This is all that quantitative chemical analysis can do. It is well to repeat the combustion with different amounts of substance. The percentage found should reasonably well agree, independent of the absolute amount taken. 41, 12.

12. The following table gives the analytical results (in per cent.) for a few TYPICAL COMPOUNDS to which we shall frequently refer:

	Carbon.	Hydrogen.	Oxygen.
1. Benzol, . . . . .	92.3	7.7	.....
2. Alcohol, . . . . .	52.2	13.0	34.8
3. Ether, . . . . .	64.8	13.6	21.6
4. Acetic Ether, . . . . .	54.4	9.1	36.5
5. Acetic Acid, . . . . .	40.0	6.7	53.3
6. Tartaric Acid, . . . . .	32.0	4.0	64.0
7. Sucrose, . . . . .	42.1	6.4	51.5
8. Urea (N 46.7), . . . . .	20.0	6.6	26.7

## 82. EMPIRICAL AND MOLECULAR FORMULÆ.

1. Several of the eight typical organic compounds for which the results of their elementary analysis are given in the preceding table we have found to sustain remarkably CLOSE CHEMICAL RELATIONS to one another (Lecture 80). This applies particularly to the four alcoholic compounds (Nos. 2 to 5). Yet the percentage composition fails to give the slightest indication of such relationship.

2. But suppose we express this per cent. composition by the chemical symbols C, H, O, N. The value of these is, respectively 12, 1, 16, 14 (40, 7). That is, let us weigh the carbon by weights of 12 units, oxygen by weights of 16 units; that is, by atomic weights. To do this, we evidently need only to DIVIDE THE PERCENTAGE BY THE ATOMIC WEIGHT.

3. The following table gives the results of this calculation, and also the simplest RATIOS of these quotients:

Compounds.	Quotient.			Ratios.		
	C	H	O	C	H	O
1. Benzol,	7.69	7.7	.....	1	1	.....
2. Alcohol,	4.35	13.0	2.17	2	6	1
3. Ether,	5.40	13.6	1.35	4	10	1
4. Acetic Ether,	5.53	9.1	2.28	2	4	1
5. Acetic Acid,	3.33	6.7	3.34	1	2	1
6. Tartaric Acid,	2.66	4.0	4.00	2	3	3
7. Sucrose,	3.51	6.4	3.22	12	22	11
8. Urea,	1.66	6.6	1.67	1	4	1
With N 3.34	.....	.....	.....	2	.....	.....

4. The simple ratios are in all cases evident, except for SUCROSE. For this substance we see that the ratio H:O evidently is 2:1. That of C:O is nearly 36:33 or 12:11, which being tried by division with 12 and 11 gives in both cases the quotient 0.29. Hence the ratios are as given. For

UREA, the only nitrogenous compound in the list, the value for this element is separately stated.

5. These ratios are all simple numbers; accordingly organic compounds conform to DALTON'S LAW of fixed, simple multiple proportions (40, Note). They represent the number of times each atomic weight must be taken to express the results of elementary analysis of the compound. Thus two C, six H and one O represents exactly the per cent. of carbon, hydrogen and oxygen found in alcohol by elementary analysis.

6. Accordingly  $C_2H_6O$  is a chemical formula representing the quantitative composition of alcohol. In the same way  $C_4H_{10}O$  represents the results of the elementary analysis of ether, and  $CH_4N_2O$  the composition of urea. These chemical formulæ are called EMPIRICAL FORMULÆ, because they express the mere fact determined by the elementary analysis of the substance.

7. Comparing the four alcoholic compounds, we see that these empirical formulæ already mark a CLOSE KINSHIP between them. They all have one oxygen only. Acetic ether has exactly double the amount of both carbon and hydrogen found in acetic acid. In alcohol the proportion of hydrogen is increased to  $\frac{3}{2}$ . In ether we find exactly the sum of alcohol and acetic ether. All for equal amounts of oxygen.

8. For volatile substances it is easy to determine their MOLECULAR WEIGHT (40, 10 to 12). Applying the method given to the volatile substances in our list, we find the following results: Benzol, 78; Alcohol, 46; Ether, 74; Acetic Ether, 88; Acetic Acid, 60. Summing up the atomic weights of the empirical formula, we find it equal to the molecular weights for alcohol and ether; half the amount for acetic ether and acetic acid; one-sixth the amount for benzol.

9. THE MOLECULAR FORMULA OF A COMPOUND REPRESENTS ONE MOLECULE OF THE SUBSTANCE—that is, the number of milligrammes of the substance which, in the gaseous state, occupies as much space as two milligrammes of

hydrogen under the same temperature and pressure (40, 10). Accordingly, the molecular formulæ are: Benzol  $C_6 H_6$ , Alcohol  $C_2 H_6 O$ , Ether  $C_4 H_{10} O$ , Acetic Ether  $C_4 H_8 O_2$ , Acetic Acid  $C_2 H_4 O_2$ .

10. The last three substances on our list are non-volatile; they decompose before they volatilize. The above method accordingly is inapplicable. Saturation of the acid by normal alkali would only give the equivalent, but not necessarily the molecule. COMBINATION WITH THE MONOVALENT SILVER is frequently sufficient. Thus when silver acetate is ignited, it leaves 0.645 silver per unit. Since  $Ag = 108$ , it follows that silver acetate is 166.8. Hence Acetate 58.8 and H Acetate 59.8 which is close to the true 60. In this manner we find tartaric is  $C_4 H_6 O_6$ .

11. A method, due to RAOULT, based upon the DEPRESSION OF THE MELTING POINT, is now quite generally used for non-volatile substances. It requires a very sensitive thermometer. We cannot here enter upon the experimental or theoretical details. The method excellently supplements the data needed for non-volatile solids. It is found that the molecular formulæ of sucrose and of urea are identical with their empirical formulæ.

12. UREA,  $CH_4N_2O$  is extracted from fresh urine. Evaporate to one-tenth its volume. Add excess of strong nitric acid: Urea nitrate appears in tabular, six-sided crystals. Separate, dissolve (purify by animal charcoal) saturate with barium hydrate solution (giving Ba Nate). Evaporate to dryness, extract with alcohol, which dissolves the Urea. Crystallize. It forms colorless (white) quadratic prisms, very soluble in water, less so in alcohol. F 132. Waste nitrogenous materials leave the body in the form of urea, about 30 grammes a day.

## 83. RADICAL AND STRUCTURAL FORMULÆ.

1. The molecular formulæ present more of the CHEMICAL RELATIONS than the empirical formulæ. Thus, the formula of alcohol and acetic acid give a sum exceeding that of acetic ether by  $\text{H}_2 \text{O}$ ; in fact, this ether is formed from the two compounds with separation of water. Again, doubling the formula of alcohol gives that of ether and of  $\text{H}_2 \text{O}$ , agreeing with the preparation of common ether. Compare 77.

2. In order more clearly to exhibit the chemical relations or reactions of the compounds, the symbols of the molecular formula should be grouped in a manner to represent the CONSTITUENT RADICALS of the compound. Thus, since alcohol,  $\text{C}_2\text{H}_6\text{O}$ , is chemically a hydrate, it must contain the monovalent negative radical  $\text{OH}$ . That leaves  $\text{C}_2\text{H}_5$  which, accordingly, must represent its positive radical ethyl. See 77, 8.

3. Consequently, the molecular formula  $\text{C}_2 \text{H}_6 \text{O}$  of alcohol should be written  $\text{C}_2 \text{H}_5 \cdot \text{OH}$ , to represent the radicals or proximate constituents of the compound, known to be present according to the chemical reactions of the substance. Such formulæ are called RADICAL FORMULÆ.

4. It is customary to connect the formulæ of the radicals by DOTS OR DASHES, as many as the valence of the same. Since  $\text{OH}$  is monovalent, ethyl must also be monovalent; accordingly a single dot has been inserted between  $\text{OH}$  and  $\text{C}_2 \text{H}_5$ . It will be readily understood that the divalent  $\text{O}$  must be marked next to the ethyl. Compare Lecture 40 and 43.

5. In ACETIC ACID,  $\text{C}_2 \text{H}_4 \text{O}_2$ , one hydrogen is replaceable by monovalent metals ( $\text{Na}$ ,  $\text{Ag}$ ); hence it stands as positive against the balance as a negative,  $\text{C}_2 \text{H}_3 \text{O}_2 \cdot \text{H}$ . This shows the formation of acetic ether  $\text{C}_2 \text{H}_5 \cdot \text{O}_2 \text{H}_3 \text{C}_2$  from alcohol  $\text{C}_2 \text{H}_5 \text{OH}$  and acetic acid  $\text{C}_2 \text{H}_3 \text{O}_2 \cdot \text{H}$  by

double decomposition with separation of water  $H. OH$  or  $H. H_2O$ . The reason for writing  $O_2$  next to  $C_2 H_5$  is evident from what has been shown above.

6. We must next inquire into the constitution of the monovalent electro positive radical  $C_2 H_5$  and the monovalent electro negative radical  $C_2 H_3 O_2$ . The tri-chloroacetic acid of Dumas (80, 3) and the production of chloroform therefrom (80, 7) will enable us to unravel the STRUCTURE OF THE negative RADICAL  $C_2 H_3 O_2$ —and thereby that of the positive  $C_2 H_5$ .

7. By chlorination of acetic acid it is necessarily the  $H_3$  in the radical that are replaced by chlorine, and not the fourth, positive hydrogen; for the chloroacetic acid saturates metals exactly as does acetic acid itself, or contains that same positive, replaceable hydrogen atom. Accordingly, TRICHLOROACETIC ACID contains the monovalent negative radical  $C_2 Cl_3 O_2$ .

8. When treated with an alkali, say  $Ka OH$ , trichloroacetic acid yields chloroform. Analysis shows CHLOROFORM to consist of carbon, hydrogen and chlorine; its empirical formula is  $CH Cl_3$ . Its molecular weight is found to be nearly 120. Consequently, its molecular formula is  $CH Cl_3$ . Hence the above radical must contain the monovalent radical  $C Cl_3$ . Accordingly it is  $C Cl_3. C O_2$ .

9. If trichloroacetic acid is neutralized with sodium hydrate and the chloroform distilled off, the residue, after proper concentration, will yield rhombic tablets. Identically the same crystals are obtained by saturating the aqueous distillate from red ants (*Formica rufa*) with sodium hydrate. The crystals accordingly are sodium FORMATE.

10. From these crystals, FORMIC ACID is obtained pure by distillation with an acid. Analysis gives the empirical formula  $CH_2 O_2$ . The molecular weight is found to be 46. It has but one  $H$  replaceable by  $Na$ . Consequently, its radi-

cal formula is  $\text{CH O}_2 \cdot \text{H}$ . When heated with concentrated sulphuric acid it yields carbonic oxide gas,  $\text{CO}$ , and water  $\text{H} \cdot \text{O} \cdot \text{H}$ . Hence it is  $\text{H} \cdot \text{CO} \cdot \text{OH}$ , for the radical CARBONYL  $\text{C O}$  is divalent.

11. The negative radical  $\text{C}_2 \text{Cl}_3 \text{O}_2$  of trichloroacetic acid has thus been found to contain the monovalent  $\text{C Cl}_3$  and  $\text{CO} \cdot \text{O}-$ . Its RADICAL STRUCTURE is therefore  $\text{C Cl}_3 \cdot \text{CO} \cdot \text{O}-$  where the last dash represents the monovalent character. Hence sodium trichloroacetate is  $\text{CCl}_3 \cdot \text{CO} \cdot \text{ONa}$ . Acetic acid accordingly is  $\text{CH}_3 \cdot \text{CO} \cdot \text{OH}$ , the last  $\text{H}$  being replaceable by metals.

12. But alcohol  $\text{C}_2 \text{H}_5 \cdot \text{OH}$  is convertible into acetic acid by oxidation. Consequently, the radical ethyl  $\text{C}_2 \text{H}_5$  contains the link  $\text{CH}_3$  as terminal; it is therefore  $\text{CH}_3 \cdot \text{CH}_2-$ . Hence the STRUCTURE OF ALCOHOL is  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{OH}$ . In this manner the radical structural formulæ of compounds are determined from their chemical reactions. The results of such determinations for five of our tabulated compounds are here appended.

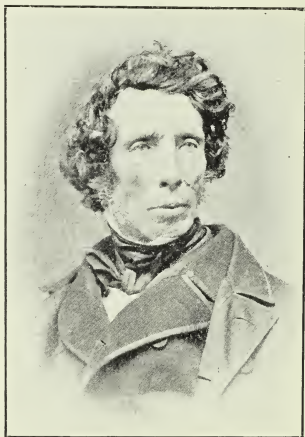
Name.	Radical Formulæ.	Structural Formulæ.
2. Alcohol, .	$\text{C}_2 \text{H}_5 \text{OH}$	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{OH}$
3. Ether, . .	$(\text{C}_2 \text{H}_5)_2 \text{O}$	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \text{CH}_3$
4. Acetic Ether, .	$\text{C}_2 \text{H}_5 \cdot \text{O}_2 \text{H}_3 \text{C}_2$	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{CH}_3$
5. Acetic Acid, .	$\text{C}_2 \text{H}_3 \text{O}_2 \cdot \text{H}$	$\text{H} \cdot \text{O} \cdot \text{CO} \cdot \text{CH}_3$
8. Urea, . .	$\text{CO} (\text{NH}_2)_2$	$\text{H}_2 \text{N} \cdot \text{CO} \cdot \text{NH}_2$

## 84. POLYMERIC AND ISOMERIC COMPOUNDS.

1. At the close of the first quarter of this century the outer walls of organic chemistry were constructed by FOUR MASTER BUILDERS on the foundation laid by Lavoisier, Gay-Lussac and Chevreul. Faraday in England, Dumas in France, Liebig in Germany and Berzelius in Sweden. In his Annual Reports

(begun 1821), the latter critically reviewed the work of the younger men:

2. Liebig had enjoyed the advantages of the French school at Gay-Lussac's. He had studied the FULMINATES there (79, 12). The empirical formula of the terrible explosive silver fulminate he found (1823) to be  $\text{Ag C N O}$ . But the same formula had been given by Wöhler for the non-explosive silver CYANATE, a year previously. Liebig, thinking that possibly an



WÖHLER.

error had been committed, repeated all analyses, but again obtained the same results. Hence two entirely different bodies are represented by the same empirical formula!

3. A few years later (1828), Wöhler, working on potassium cyanate,  $\text{K O Cy}$ , found that by heating a mixture of equivalent solutions of this salt and of ammonium sulphate,  $\text{Am}_2 \text{O}_4 \text{S}$ , the dry residue, upon extraction with alcohol, gave CRYSTALS OF UREA. (72, 12). Double decomposition yielded



difficultly soluble Ka Sate; the other compound, Am O Cy had evidently changed into Urea.

4. Writing out the radicals Am and Cy, the ammonium cyanate is represented by the formula  $\text{NH}_4 \text{ O. CN}$ , while urea (83, 12) is represented by  $\text{H}_2\text{N. OC. NH}_2$ . Evidently, the hydrogen has changed place, and carbon and oxygen have combined more intimately, nitrogen and carbon less so, the nitrogen now being partly saturated by the additional hydrogen. This has been called a synthesis of urea; but it is simply an "ATOM WANDERUNG."

5. About the same time (1825) Faraday discovered the liquid hydrocarbon BENZOL (62, 6) in coal tar. On analysis he found C H as the empirical formula. He was amazed at this result, because the same formula was considered to represent the gas called olefiant gas, obtained by gently heating the mixture of one volume of alcohol and six volumes of concentrated sulphuric acid.

6. Berzelius for several years supposed these results to be erroneous. But while investigating TARTARIC ACID and tartrates (1831), he discovered that RACEMIC ACID had exactly the same quantitative composition as tartaric acid, the analyses of both leading to exactly the same empirical formula. Now he admitted the facts stated and coined the names still in use: polymeric and isomeric compounds.

7. In the terms of the present, different substances, having the same percent composition, and therefore expressed by the same empirical formula, are either POLYMERIC or ISOMERIC, according as their molecular formula is different or identic. In the latter case, the radical formulæ differ.

8. The empirical formula of olefiant gas now is known to differ from that of benzol; it is  $\text{CH}_2$  and not CH. But ACETYLENE (which Berthelot obtained by direct synthesis, forty years ago, and which now is produced in quantity by Moissan from his calcium carbide and water) has identically the same percentage composition as benzol, and therefore the same empirical formula CH.

9. The molecular weight of benzol is 78 (82, 8), but that of acetylene is found to be 26 only. Accordingly, while the molecular formula of benzol is  $C_6H_6$  (82, 9), acetylene is represented by the molecular formula  $C_2H_2$ . — It thus appears that a benzol molecule weighs three times as much as a molecule of acetylene. Berthelot has indeed, CONDENSED ACETYLENE TO BENZOL by passing it through a red hot tube. He has also decomposed benzol into acetylene.

10. The empirical formula  $Ag\ C\ N\ O$  represents both silver cyanate  $Ag\cdot O\cdot CN$  and silver fulminate  $Ag_2:C:\overset{a}{b}$  where  $a$  stands for  $O_2N$  and  $b$  for  $CN$ . These compounds are isomeric. The radical formulæ for ammonium cyanate and for urea have been given in 4; these compounds are isomerics, represented by their common empirical formula  $CH_4\ N_2\ O$ . The case of tartaric and racemic acids is of a higher order, and will be considered in the next lecture.

11. Since the masters brought the nature of isomerism and and polymerism to light, these phenomena have been found to be common among organic compounds. Thus the molecular formula of ETHER,  $C_4H_{10}O$  represents quite a number of different isomerics. Among the most common of these is BUTYL ALCOHOL,  $C_4H_9.OH$  or  $CH_3.CH_2.CH_2.CH_2.OH$ . It is a liquid (obtainable from butyric acid) of pleasant odor, requiring 12 volumes of water for solution.  $G\ 0.81$  (at 20),  $B\ 117$ . Nobody could possibly confound such a liquid with ether; yet it has not only the same empirical, but even the same molecular formula.

12. In view of these facts, it is manifest, that the empirical, and even the molecular formulæ of compounds, are of comparatively little value; they really give no insight into the chemical nature of the same, for they each one apply to many entirely different isomeric or polymeric compounds that often could not be confounded by the merest tyro. THE CHEMICAL NATURE OF COMPOUNDS IS EXPRESSED IN THEIR RADICAL AND STRUCTURAL FORMULÆ.

## 85. RIGHT- AND LEFT-HANDED COMPOUNDS.

1. Further study of isomerics has revealed the existence of compounds containing exactly the same chemical radicals and yet so different, one from the other, that not only man, but even monads readily can distinguish them. The case of tartaric and racemic acid of Berzelius is the first instance of this kind. 84, 6.

2. Recent researches have shown that these compounds differ one from the other as does the glove of the right-hand from that of the left. Though both hands are identical in most respects, they are not equal, but symmetric—the one is exactly like the reflected image of the other. Chemical compounds of this kind are designated as LEFT- (l) and RIGHT (d, dextro) -HANDED modifications or geometrical isomerics.

3. These differences are by no means hard to recognize. When crystallized, the substances show it to the unaided eye. When in solution, they show it so plainly in POLARIZED LIGHT that one of the most common methods of analysis of organic compounds is based upon this difference (45, 6). Common officers of the civil government determine import duty and credit bonus on sugar by this method of polarization. Even monads will eat the one and refuse the other of these isomerics.

4. THE HISTORY of this line of research is both fascinating and instructive. If we could give a lecture course on this subject instead of a single lecture, we would have ample material to sustain the interest 'till the close. The researches leading to these wonderful results also sharply mark the difference between routine work of detail and the discoveries due to genius. The masses never can do the work of the master.

5. The now popular method of SPECIAL RESEARCH imported, duty free, with cheap parchments, is as impotent as the empty formula of Bacon and the hairsplitting verbiage of the scholast. On the contrary, we see the work of physicist (Biot) astronomer (Arago, Sir John Herschel) crystallographer (Haüy, Mitscherlich) and chemist (Berzelius, Pasteur) concentrated in the one final result under consideration.

6. To approach this subject understandingly, we must, for the moment, leave our ethers and acids with the chemists and examine once again the quartz crystal with the physicist and crystallographer. ARAGO had discovered (1811) that it turns the plane of polarized light, passing parallel to its axis. BIOT had found that this rotation is exactly proportional to the thickness of the plate, and that many organic compounds (sugars, volatile oils, alkaloids) possess the same property.

7. The most important forms of the crystals of quartz are represented on the upper part of p. 65. The dominant prism  $r$  and rhombohedræ  $P$  and  $z$  have been described (10, 6). Close inspection had already shown HAÜY the rhombic facets  $s$  and the (plagihedral) trapez facets  $x$  in the zone-like belt  $P$   $s$   $x$   $r$  (fig. 5). The angles are  $Ps$  151.1,  $r$   $x$  168.0 and  $s$   $r$  142.0. The rhombic facets generally show a high luster, and may be striated parallel to edge  $Pr$  (figs. 6, 7). The facets  $x$  are usually dim.

8. The astronomer SIR JOHN HERSCHEL, in 1820, discovered that in right-handed quartz (upper  $P$   $s$   $x$   $r$  to right, fig. 7) the polarized ray of light is turned to the right, while in left-handed quartz ( $P$   $s$   $x$   $r$  to left, fig. 6) the light is turned in the opposite direction. We now use plates of such crystals in finer polarizing microscopes. The order of succession of the colors on turning the analyzer indicates the nature of the crystal, whether right- or left-handed.

9. Solutions of tartaric acid show polarization while solutions of the isomeric racemic acid show none. But PASTEUR (1848) found that ammonium-sodium racemate gave on

crystallization, crystals showing similar plagihedral facets, either to the right or to the left of certain main forms, precisely as we find it in quartz. Picking these crystals by hand, separating the acids by Scheele's method (63.2) and dissolving these separately, he obtained from the non-active racemic acid both a right-handed and a left-handed acid. The first is identical with tartaric acid.

10. Accordingly, RACEMIC ACID is merely a combination of *r* (old) and *l* (new) tartaric acid. Pasteur demonstrated this conclusion by synthesis, which took place with notable evolution of heat. The compound resulting was racemic acid. The molecular formula of tartaric acid  $C_4H_6O_6$  indicates none of these relations. It is dibasic, containing twice  $CO.OH$ . Radically it is  $HO.CO.CHX.CHX.CO.OH$  where *X* stands for hydroxyl  $OH$ . Non-active isomerics are marked *i* (inactive). Doubled (neutral), meso.

11. Now all the formulæ of organic compounds given show plainly that carbon may be considered quadrivalent; compare also 40, 4, 5. Remembering this, the formula just quoted shows tartaric acid to contain two carbon atoms each combined mutually and with the monovalent  $H$ ,  $OH$  marked *X* and  $CO.OH$ , the weights of which are 1, 17, 45. The fourth valence holds exactly half the entire compound, or 75.

12. In other words, each one of the central carbons is combined or loaded with the weights 1, 17, 45, 75, all four unequal. The load is entirely unsymmetric. A carbon atom so combined is called ASYMMETRIC by VAN'T HOFF (Holland, 1874) and LE BEL (France, 1874), who independently generalized this condition: No rotary polarization without at least one asymmetric carbon atom.

---

PASTEUR BEFORE BIOT. The research here reported was the first one made by Pasteur, submitted to the Academy of Sciences of Paris. The old investigator of rotary polarization, Biot, was to report on the merit of the work of young Pasteur. The following is a synopsis of the

account of the examination made by Biot, as reported by Pasteur himself in his Lecture on January 20th, 1860, before the Chemical Society of Paris:

"Biot requested me to call on him and to repeat my experiments in his presence. He gave me racemic acid, which he had himself optically examined, and found to be entirely inactive. I converted this in his presence, into the Ammonio-Sodium salt, using the ammonia and soda furnished by himself (Biot). The solution was set aside in his laboratory for spontaneous evaporation. When 30 to 40 grammes of crystals had separated, he again requested me to call at the College de France, in order to pick out, under his very eye, the right- and left-handed crystals. He asked me to repeat the declaration, that the crystals which I should place to his right would, in solution, turn the polarized light to the right, and those which I should place to his left would deflect the ray to the left. After I had done the work accordingly, he said that he would himself do the rest. He carefully prepared the solutions from weighed quantities, and when he was ready to make the final observation by means of the polarizing apparatus, he called me again into his room. He first put the most important solution into the apparatus, namely the solution which was to deflect to the left. Without taking a reading, at the mere aspect of the tints of color in the two-halves of the field (of the Soleil Saccharimeter) he instantly recognized the presence of a deflection to the left. The gray-haired man was profoundly moved; he grasped my hand and said: My dear boy, I have loved science all my life so much that I hear my heart beat for joy at this sight."

We may, with Pasteur, call attention to the fact that Biot had, for twenty years, urged chemists to study rotary polarization as a means of investigating the structure of chemical compounds. Pasteur was the first who did so and was richly rewarded. Strange as it may seem, this very research led him directly to his wonderful biological discoveries which now dominate medicine (71. 11). For searching for methods of separation of these right- and left-handed substances, which deport themselves alike to all chemical reagents, he naturally tried the action of ferments. Now tartrates were known to ferment readily. Accordingly he added this ferment to a solution of ammonium racemate, to which the necessary albumin had been added as ferment-food (71. 4). The liquid was placed in the tube of his polarizing apparatus. Racemate being inactive, no deflection was seen at the beginning. But as the fermentation spread, the plane of polarized light turned towards the left. The ferments (from right-handed tartrates) consumed this right-handed tartrate of the ammonium racemate. The left-handed portion was not attacked—and caused the turning of the plane of polarized light.

The ox eats no flesh and the lion refuses to eat grass. To the ferment cells of right-handed tartrates, the left-handed isomeric evidently appears as different as do flesh and grass to the higher animals.

## 86. TETRAHEDRON AND BENZOL RING.

1. Modern scientists frequently deride the views of the philosophers of Ancient Greece on the constitution of things. The use of the regular polyhedrae by Plato (Timæos) is a favorite topic of this kind. Nevertheless, the chemical literature of to-day places PLATO'S TETRAHEDRON at the head of the science. It has become the nucleus of all organic compounds. It is  $\text{CH}_4$ .

2. When Van't Hoff and Le Bel had recognized the asymmetric carbon, they both concluded that the four hydrogen atoms of  $\text{CH}_4$  occupy the corners and the carbon atoms the center of a regular tetrahedron. In series; these TETRAHEDRAE WERE STRUNG along a line, corner to corner, independent of the fundamental laws of mechanics.

3. THE PUZZLE of placing three hundred soldiers on the ramparts of a square fort so that each side shall be defended by one hundred men is commonly solved by placing fifty in the middle of each side and twenty-five at each corner. Such solutions answer the purpose of a puzzle admirable till the enemy attacks all sides at once. As reward for this puzzle-solution, Van't Hoff was called from Holland to the chair of chemistry in the University of Berlin, Germany.

4. It is only after almost fifteen years that the mechanical absurdity of this stringing of tetrahedrae was recognized. The utter absence of scientific understanding in the highest circles of German chemistry is strikingly evidenced by the report in Bischoff's Big Book (1894) on Stereochemistry; 1060 pages only. He simply prints (p. 79) both pictures; the one marked "jetzt" and the other marked "früher." No comments. "ALLES WURST."

5. If the "latter view" of Van't Hoff is taken, the alcoholic compounds necessarily have a CORKSCREW STRUCTURE. This structure of alcoholic compounds would seem to be emi-

nently appropriate to those who know alcohols numbers two and five only. Really, the theory demands no serious consideration here. See my paper, *Comptes Rendus*, T. 113, p. 745; 1891.

6. Ostwald (1896) in his *History of Electro-Chemistry* (only 1,152 pages, mostly reprints) repeatedly castigates German scientists of a preceding period for succumbing to the disease "Naturphilosophie." In a near future, the chemists of the present age will probably be said to have succumbed to the TETRAHEDRAL BACILLUS.

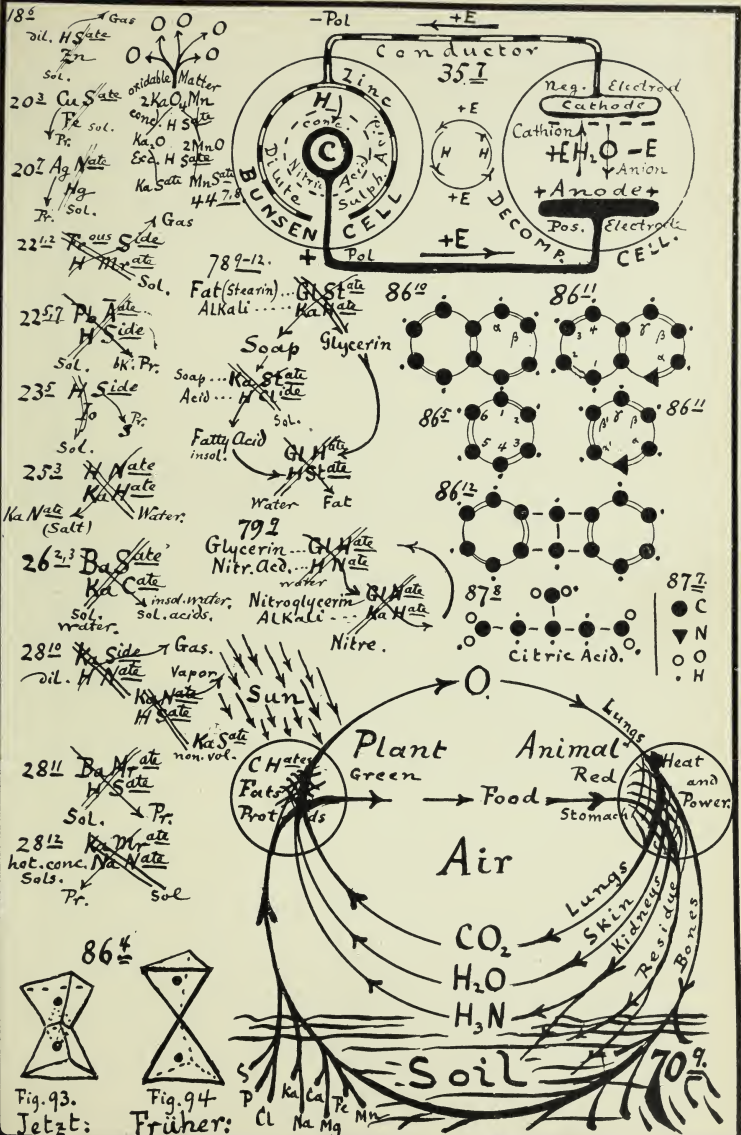
7. There is another, and considerably older picture in modern chemical literature. It is the HEXAGON, introduced by Kekulé (1866) to represent the constitution of BENZOL,  $C_6H_6$ . The six carbons are supposed to form a hexagon and to be tied alternately singly and doubly, and outwardly combined with one hydrogen each. Thus the four valencies of each carbon are supposed to be saturated. See diagram.

8. This view has rendered undoubted services to the progress of chemical science. It has been frequently attacked, also on thermochemical grounds by Thomsen, of Copenhagen. Prismatic and other more elaborate formulæ, have been presented as substitutes. The solution of Kekulé appears to represent all facts known. That IT IS IN ACCORDANCE WITH MOLECELAR MECHANICS we have shown in our *Principles of Chemistry*, 1874, and in the *Comptes Rendus*, 1875.

9. The relations between BENZOL AND ACETYLENE, discovered by Berthelot (84, 9) are strong facts in favor of this ring-form. The formula resolves itself in the same three parts, held by a double tie. Each of these parts represents one of acetylene. This indicates also that the carbon atoms really do not form a regular hexagon, but correspond in position to the rhombohedron.

10. NAPHTALENE (74, 2) is a condensed form of benzol; two atoms united under loss of two carbons. The accepted







constitution is shown in the diagram given. The two carbons common to the two benzol rings are tied doubly; hence only four carbons in each ring can unite with hydrogen. The formula for naphtalene must be  $C_{10}H_8$ .

11. The trivalent nitrogen may take the place of one carbon in either benzol or naphtalene. Being trivalent it cannot combine with an outer hydrogen, so that these compounds contain respectively 5 and 7 hydrogen only.  $C_5 N H_5$  is called PYRIDINE (74, 10) and  $C_9 N H_7$  is CHINOLINE (74, 11). See diagrams given.

12. Many higher condensations exist. Thus ANTHRACENE (74, 3) is considered to result from two complete benzol rings tied rather curiously by 2 CH as shown in the diagram. The structure looks like three benzol rings, the middle of which has a diagonal tie. Formula  $C_{14} H_{10}$ . These forms are the only ones that require attention.

## 87. ALCOHOLIC COMPOUNDS.

1. The general chemical principles exposed in the preceding lectures were obtained in the study of the compounds extracted from the most common organic prime materials. We will now take a look at the principal CLASSES OF COMPOUNDS. A detailed systematic exposition of organic compounds must be looked up in any of the numerous manuals.

2. All organic compounds may be roughly arranged in THREE GREAT DIVISIONS. Aromatic compounds contain the benzol ring. Alcoholic compounds do not contain such a ring. Complex compounds may contain both alcoholic and aromatic radicals.

3. Of true alcoholic compounds, the acids have always been most prominent. Scheele and Chevreul opened the way in this investigation. We have seen that all these acids con-

tain the radical carboxyl CO united to hydroxyl OH. That is, acids contain the TERMINAL  $\text{--CO.OH}$  or summarily  $\text{--CO H}$ . The dash indicates that this terminal is monovalent.

4. In formic, acetic, butyric, palmitic and stearic acids we find this acid-terminal only once; these acids are called monobasic. In oxalic and tartaric acids, this terminal occurs twice; they are said to be dibasic. In tribasic citric acid this terminal occurs three times. These are about the only alcoholic acids specially studied in the preceding. The NUMBER of times this terminal occurs in any acid determines the SATURATING CAPACITY of that acid.

5. If we determine the formulæ of the radicals united with this terminal in the first five acids enumerated, we find them to be H,  $\text{CH}_3$ ,  $\text{C}_3\text{H}_7$ ,  $\text{C}_{15}\text{H}_{31}$ ,  $\text{C}_{17}\text{H}_{35}$ . For any number  $m$  of carbon atoms, these monovalent alcohol radicals are seen to contain twice that number of hydrogen atoms and one over ( $2m + 1$ ). The ALCOHOLIC RADICAL  $\text{R}_m$  is therefore expressed by the general formula  $\text{C}_m\text{H}_{2m+1}$ .

6. Oxalic acid is that terminal united with itself or  $\text{HO.CO--CO.OH}$ . The formula of tartaric acid has already been given (85, 10). CITRIC ACID (63, 5) contains the acid terminal  $\text{--CO.OH}$  three times, being united to each carbon of the trivalent alcohol radical  $\text{CH}_2.\text{CH}.\text{CH}_2$ . Formulæ of this kind become rather complex when written out in full, and are especially difficult for the printer. Hence we only have given the radicals, separately.

7. It is much preferable to REPRESENT COMPLEX FORMULÆ GRAPHICALLY. To avoid too great specialization we represent the atoms by circles or disks. The tetravalent carbon by a large, black, the divalent oxygen by a smaller open circle, and the monovalent hydrogen by a dot. The trivalent nitrogen we represent by a triangle. If ties are to be marked, they may be represented by straight lines as usual.

8. THE DIAGRAM and fully written out formula of citric acid will once for all show the advantages of this representation of organic compounds (see plate). We wish to insist that these diagrams are merely to be taken as graphic formulæ which it is much easier to write and to read than the complex, fully written out DEVELOPED FORMULÆ of the books that are the despair of the compositor and the student.

9. By strong reducing agents—such as nascent hydrogen produced by sodium amalgam in the open, or hydriotic acid in the autoclave—THE ACIDS CAN GENERALLY BE REDUCED TO AN ALCOHOL. In that case, the carbonyl CO is reduced to CH<sub>2</sub>. Thus acetic acid CH<sub>3</sub>.CO.OH yields common (ethyl) alcohol CH<sub>3</sub>.CH<sub>2</sub>.OH. This process is quite general and reversible. Alcohols, by oxydizing agents, are converted into acids (77, 1).

10. ETHERS ARE EITHER OXIDES OR SALTS. The first may be compared to water H<sub>2</sub> O or H.O.H in which the hydrogen is supposed to be replaced by two monovalent alcohol radicals. These are the same in simple, different in mixed ethers. Examples Et. O. Et and Et. O. Me, where Me represents methyl CH<sub>3</sub>. The ether salts contain an acid radical and an alcohol radical. Example, acetic ether, Et. O. Ac where Ac stands for acetyl. CH<sub>3</sub>.CO—.

11. AMINES AND AMIDES may be compared to ammonia NH<sub>3</sub> exactly as ethers to water. In amines, the hydrogen of ammonia may be supposed to have been replaced by alcohol radicals; in the amides we have one or more acid radicals. Thus ethyl amine Et N H<sub>2</sub> and acetyl amide Ac N H<sub>2</sub> (Acetamide). The latter is a crystalline solid, F 75, B 222; the former is a very limpid, ammoniacal liquid, G 0.7, B. 18.4. Urea is simply CARBAMIDE (82, 12). A. W. Hofman (p. 34) worked this field very successfully and gave German chemistry that industrial character it has since retained.

12. ALDEHYDES (80, 9) are intermediate between acid and alcohol; they contain the monovalent terminal —COH.

KETONES contain carbonyl united with two alcohol radicals  $R$ ,  $R'$ ; they may be considered as ethers in which the oxygen has been replaced by carbonyl. Their general expression is, accordingly,  $R\text{-CO-}R'$ . If  $R = R' = \text{Me} = \text{CH}_3$  we have acetone,  $\text{CH}_3\text{. CO. CH}_3$ . 75, 12.

## 88. AROMATIC COMPOUNDS.

1. The aromatic compounds more READILY UNDERGO SUBSTITUTIONS than the alcoholic compounds. The benzol ring is wonderfully ready to exchange its hydrogen. Furthermore, the grouping of the carbons in the ring gives rise to an almost infinite number of isomerics.

2. Treating benzol (62, 6; 74, 1) with the mixture of concentrated nitric and sulphuric acid (79, 8). we do not obtain a saponifiable nitrate, but NITRO-BENZOL. Investigation has shown that benzol exchanges one hydrogen for the monovalent radical nitryl,  $\text{NO}_2$ . At the same time, the hydrogen is oxidized to water.  $\text{C}_6\text{H}_6$  thus changes to  $\text{C}_6\text{H}_5\text{.NO}_2$ . The monovalent radical  $\text{C}_5\text{H}_5$  is called phenyl; for it exists in phenol. It may be represented by Ph.

3. NITRO-BENZOL,  $\text{Ph. NO}_2$  is a yellowish liquid, of the odor of oil of bitter almonds, for which it is substituted in cheap perfumes. G 1.3, F 3 (solidifies) B 220. Acted upon by nascent hydrogen (from iron and acetic acid) it is reduced to ANILINE,  $\text{Ph. NH}_2$  (74, 12), which really is prepared in this manner from benzol for the manufacture of aniline colors.

4. Crushed bitter almonds ferment upon the addition of water, and yield a distillate which gives a crystalline precipitate with sodium bisulphite. Accordingly, it contains an aldehyde (80, 10) which is separated from the crystals by means of sodium hydrate, and purified by rectification from calcium chloride. It is called BENZALDEHYDE and is found (Woehler, 1832) to be  $\text{Ph. COH}$  (compare 87, 12).

5. BENZALDEHYDE, Ph. COH, is a colorless, highly refractive liquid, of a pleasant, characteristic odor and an aromatic taste. 1.07 at 0, B 179.5. By moderate heat it gives benzol Ph H and carbonyl CO gas. Exposed to the air and sun light, this aldehyde changes to its acid (87, 12), namely benzoic acid, Ph.CO.OH, which see (62, 7).

6. PHENOL (74, 6) upon analysis is found to be Ph. OH or phenyl hydroxyl. It can be obtained, by a somewhat circuitous way, from benzol. By dropping melted phenol into boiling nitric acid, tri-nitro phenol  $C_6H_2(NO_2)_3 OH$  is obtained, commonly called carbazotic or PICRIC ACID. It forms yellow lamellar crystals, difficultly soluble in water. On sudden heating it explodes. Its salts are very explosive. It dyes yellow a thousand times its own weight of silk.

7. This and other nitro-phenols, when reduced, give amido-phenols. The ethyl ethers hereof are called phenetidins. One of these treated with glacial acetic acid yields the modern synthetic remedy PHENACETIN, forming shining crystals, without odor and almost without taste; F 135. It is an antipyretic. Chemically it is acet-para-phenetidin,  $C_6H_4 A B$ , where A stands for  $-O.C_2H_5$  and B for  $-NH(C_2H_5O)$ .

8. After much research it has been ascertained that phenol with one nitryl gives three distinct isomerics, called ORTHO-, META- and PARA-NITRO-PHENOL, or designated more briefly by the initials o, m and p. It has further been ascertained, that counting from the carbon combined with hydroxyl in phenol, ortho compounds have the second, meta the third and para the fourth carbon combined with nitryl. See diagram.

9. Each of the other aromatic hydrocarbons gives series of compounds corresponding to the benzol compounds here barely hinted at. Furthermore, the number of isomerics rapidly increases with the complexity of the hydrocarbon. Thus naphthalene (74, 2) gives, when one hydrogen is replaced by hydroxyl, the two NAPHTOLS (74, 8) which are isomeric; both expressed by the same formula  $C_{10}H_7.OH$ .

10. If a hydrogen atom next to one of the two carbon atoms, common to the two benzol rings, has been replaced, it is the  $\alpha$ -naphthol. If the outer hydrogen atom has been replaced, the  $\beta$ -naphthol results. How chemists have finally determined these questions of PLACE IN THE ATOM is a matter entirely for special study and altogether beyond the scope of this introduction. How these results are confirmed and established by mechanical laws will be indicated in the last ten lectures of this course.

11. Still more numerous are the isomerics obtained by substitution in pyridine and chinoline (86, 11 and 74, 10, 11). Ladenburg succeeded (1888) in combining normal-propyl,  $\text{CH}_3.\text{CH}_2.\text{CH}_2-$  in the  $\alpha$ -position (i. e. next to the nitrogen) in piperidine (74, 10); the product was identical in all chemical reactions and in rotary polarization (right-handed) with true coniine (64, 12). He had accomplished the SYNTHESIS OF AN ALKALOID, the first on record.

12. PHENYLHYDRAZINE  $\text{Ph. HN.NH}_2$  is now an important reagent for aldehydes and sugars. It is made from aniline by a somewhat complex process. It is a colorless oil (G 1.19) of a peculiar odor, solidifying to tabular crystals that fuse at 17, 5. It forms a hydrate melting at 24. The liquid turns brown on exposure. Its crystallized hydro chloride keeps well. One part hereof dissolved with one-and-a-half parts of sodium acetate in 8 to 10 parts of water is the glucose reagent used.

## 89. COMPLEX COMPOUNDS.

1. In my PRINCIPLES OF CHEMISTRY AND MOLECULAR MECHANICS, published a quarter century ago, the chapter on complex compounds (pp. 88-102) comprises mainly the saccharine bodies, the alkaloids and the albuminoids. The structure of these compounds has been greatly cleared up dur-



ing the interval; even the albuminoids have yielded to the labors of Schützenberger, of Paris.

Beholding the infinite extent of this branch of chemistry, and overcome by the difficulty of giving a reasonably fair conception thereof to the mind of my reader or hearer, within the narrow limits of the chapter or the hour, I select, as only subject for this lesson, the cup that cheers but does not inebriate. 64, 4.

2. More than five hundred million pounds of dried TEA LEAVES are used by man every year, and the weight of COFFEE BEANS consumed is very much greater still. In South America, MATE and GUARANA correspond to tea and coffee. The KOLA nut of Africa has similarly been used and has now found its way to us. Why do millions of men, in all climes, labor to enjoy a cup of these drinks? And what about the drink of the old Mexicans that inspired Linnæus to name the tree THEOBROMA?

3. When Sertuerner had succeeded to extract the active principle of opium (64, 7-8), chemists began their investigation of the question just asked. The answer is not yet complete; but the researches undertaken and the results obtained are so characteristic of the CHEMISTRY OF COMPLEX COMPOUNDS that we shall restrict ourselves here to this single topic.

Runge (1820) extracted the active principle of coffee, the glistening, acicular crystals of CAFFEINE. Robiquet, Pelletier and Caventou produced the same substance about the same time. In 1827, Oudry extracted the active principle of tea, and called it THEINE. In 1840, Martins found caffeine in Guarana, and Stenhouse found (1843) theine in maté. Lam-padius found in cacao a substance similar to caffeine (Berzelius); it is now called THEOBROMINE.

While extracted like alkaloids, these three substances are not poisonous and not strictly alkaloids; at least they are not precipitated by the general alkaloid reagents. They are largely combined with tannin—especially in tea. When the

hot aqueous extract is precipitated by basic lead acetate, the excess of lead separated from the filtrate by hydrogen sulphide, and the liquid carefully evaporated to dryness, hot alcohol will extract the alkaloidal substances in question and leave them in crystal form.

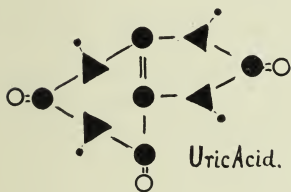
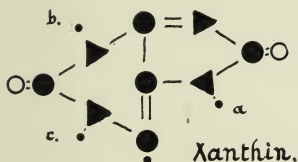
4. The noted Dutch chemist, Mulder, showed (1838) that THEINE AND CAFFEINE ARE IDENTICAL bodies in every respect. If, as some contend, tea is a protestant and coffee a catholic drink, the difference must reside in associate materials and not in the essential or active principles of these substances which, like the fundamental principles of religion, are the same in both.

Chemists were treated to another surprise when THEOBROMINE, by treatment with methyl iodide in the autoclave, was CONVERTED INTO THEINE, which thus appears as methyl-theobromine. This change was already indicated by the elementary analysis, which had given, for theobromine  $C_7 H_8 N_4 O_2$  and for theine (caffeine)  $C H_{10} N_4 O_2$ . The excess  $CH_2$  points to the additional link or methyl.

5. When either of these active substances of tea, coffee or chocolate is heated on the water bath with a strong oxidizer (nitric acid, chlorine water) to dryness, a yellowish residue remains, which dissolves in the least possible amount of ammonia with a beautiful purple color. But this is the familiar MUREXIDE TEST, commonly used for the identification of uric acid.

6. URIC ACID, being slightly soluble in water, gradually separates from urine in crystals of characteristic forms, upon the addition of the very soluble muriatic acid. By dissolving the reddish crystals in alkali, discoloring with bone black, and reprecipitating by a soluble acid, we obtain uric acid in beautiful, colorless rhombic crystals. It is insoluble in alcohol and ether, difficultly soluble in water (1 in 15,000). This lack of solubility causes gouty and rheumatic troubles. Piperazine is the best internal solvent for uric acid.

7. MUREXIDE is ammonium purpurate. With one atom of water it forms quadratic crystals  $[C_5 H_4 (NH_4) N_5 O_6 + H_2O]$  reflecting golden and greenish colors in sun light and dissolving in water to a rich purple color. It has been extensively used as a dye. Boiling destroys it under evolution of ammonia gas. Guano, being largely uric acid and urates, permits the preparation of murexid in quantity.



In the extract of tea leaves we find a correlated nitrogenous body, which does not show the murexid reaction, but instead gives the XANTHIN reaction. That is, when evaporated with nitric acid to dryness, it turns YELLOW to yellowish red with potassa, and thereafter purplish on heating. The same substance, Xanthin, occurs in the animal system. Its formula is  $C_5 H_4 N_4 O_2$ , that of uric acid being  $C_5 H_4 N_4 O_3$ . The latter seems to be an oxide of the former.

8. Comparing THE MOLECULAR FORMULÆ of the four compounds before us, and simply giving the number of atoms of C, H, N, O invariably in this order, we find: Uric acid, 5, 4, 4, 3; Xanthin, 5, 4, 4, 2; Theobromine, 7, 8, 4, 2; Theine, 8, 10, 4, 2. Accordingly, uric acid might be oxidized Xanthin. Theobromine contains 2  $CH_2$  and Theine 3  $CH_2$  more than Xanthin.

9. Long-continued and difficult chemical researches, both analytical and synthetical, have shown these substances to be actually related in that way. Analytically, all THESE COM-

POUNDS YIELD UREA  $\text{H}_2\text{N}-\text{CO}-\text{NH}_2$ ; in fact, each yields two molecules per atom when completely broken up. Accordingly, each one of these four substances contains two nuclei of urea. Synthetically, the three bodies have now all been made from Xanthin.

10. One of the four urea nuclei (the one to the right in the diagrams) is split off much more readily than the other; the two are therefore not tied or bound in the same manner. In many cases—such as the oxidation in the murexid test—the other urea nucleus (to the left) remains united with a group  $\text{C}_3$  to ALLOXAN. This Group  $\text{C}_3$  is separated as mesoxalic acid  $\text{C}_3 \text{H}_2\text{O}_5$  when alloxan is boiled with baryta water.

11. Emil Fischer, of Berlin, has completed the synthesis of these substances (Naturw-Rundschau, 1896, p. 245) in conformity with the results of decomposition here indicated. His investigations are expressed in the graphical formulæ here inserted. These diagrams have been constructed according to the developed structural formulæ published by him. Theobromine is dimethylxanthin, the methyl  $\text{CH}_3$  taking the places of hydrogen at a and b. Theine is trimethylxanthin, containing an additional methyl instead of the hydrogen atom at c.

12. And now, DO WE UNDERSTAND THE CRAVING OF MAN FOR TEA, COFFEE AND CHOCOLATE? By no means. But we have seen how complex organic compounds are being taken to pieces, and built up again. Also, how a small amount of certain substances may exert great influence on the body and how near the most refined food approaches some of the waste products of the system. Do they perform the function of the lubricant in the humon machine? The deeper we search, and the more we learn, the greater becomes the mystery to the thinker. Every question answered raises at least one new question, more profound and much more difficult than the one just answered.

## 90. ORGANIC SYNTHESIS.

1. In this lesson we reach THE PRESENT BOUNDARY OF CHEMISTRY. We have begun our course with the prime materials furnished by plant and animal. We have extracted the pure chemical compounds thereof. We have changed and transformed these in many ways. We have been enabled to learn much of the intimate structure of these bodies.

2. Chemists have produced NEW SUBSTANCES, constructed on exactly the same plan as these organic substances, but such as nature never had produced because they cannot even exist under ordinary conditions. The chemist had not only to create these compounds, but also to protect them against surrounding nature. We refer to the ORGANO-METALLIC COMPOUNDS.

3. Bunsen's researches (1842) on arsenic radicals (cacodyl, —  $\text{As Me}_2$ , monovalent) opened this field. Frankland produced (1849) quite a group of simple ethers containing heavy metals instead of oxygen, such as zinc ethyl,  $\text{Zn Et}_2$ . In 1869 FRIEDEL began his extended researches, establishing a CHEMISTRY OF SILICON COMPOUNDS parallel to that of the carbon compounds or organic chemistry, including silicon chloroform and ethers, and determining the true constitution of all silicon compounds, from that of quartz onward!

4. These organo-metallic compounds almost invariably BURN IN CONTACT WITH THE ATMOSPHERE. They have to be prepared and maintained in an artificial atmosphere free from oxygen. Their preparation is both DIFFICULT AND DANGEROUS. The lessons they have taught are most important. See my paper on Central Substitution, *Comptes Rendus*, T. 115, p. 314; 1892.

5. In the chemical changes of true organic compounds, that is, such as have been extracted from vegetable and animal materials, as well as in the formation of organo-metallic compounds, no really new reactions have been resorted

to or discovered. ALL ORGANIC CHEMICAL REACTIONS ARE IN NO MANNER DIFFERENT FROM THOSE OF INORGANIC CHEMISTRY. The forces brought into play being less, and the compounds being generally more complex, greater delicacy in the chemical operations is ordinarily essential to success.

6. Hence it would seem that any true organic compound, as produced in the living plant or animal, ought to be producible in the chemical laboratory by SYNTHESIS FROM INORGANIC MATERIALS, provided the chemist be skillful enough and provided he possess sufficient knowledge. But as a matter of fact, no truly organic compound had been produced by synthesis from the elements up to the middle of this century.

7. At that time LIEBIG was considered the leading chemist of the world. In his "Chemical Letters" of 1844 he DECLARED IT IMPOSSIBLE to produce any organic compound from the constituent elements. These letters had a wide circulation in all countries, having been translated into most languages.

8. Liebig was well aware that his friend and oft-time collaborer Woehler had produced (1828) UREA from inorganic materials (84, 4). This compound was, however, looked upon as an organic waste product merely; besides, the cyanogen compounds used in the transformation might be considered either organic or inorganic themselves.

9. Liebig's declaration would have been in exact accordance with fact, if he had said it was "impossible for him" to produce organic compounds by synthesis from the elements. He erred in assuming that what was impossible for him would also be impossible for all other chemists, and forever!

10. The man who was soon to do what Liebig declared an absolute impossibility was already studying chemistry at Paris. Six years later he became attached to the Collège de France as an assistant. Ten years after the declaration of Liebig, he

had accomplished one of the impossibilities of Liebig, the synthesis of the fats (78, 12). In 1860, the Impossibility of Liebig was replaced by BERTHELOT'S ORGANIC CHEMISTRY FOUNDED ON SYNTHESIS.

This work has so completely changed the aspect of chemical science, that it is unnecessary to enter upon details. His method of operation, as well as of thought, have become part of the science. A most fascinating exposition thereof has been given by Berthelot himself in his CHEMICAL SYNTHESIS, Paris, 1876; a volume forming part of the International Scientific Library.

11. The most brilliant work of chemical synthesis done in Germany has been accomplished by EMIL FISCHER, now at the University of Berlin. His discovery of the reaction of glucose on phenylhydrazin (88, 12) furnished him the instrument that lead to THE SYNTHESIS OF ALL THE SUGARS. His admirable work on uric acid and the allied compounds has been considered in our preceding lesson.

12. And now—WILL SYNTHESIS FROM INORGANIC MATERIALS EVER DO AWAY WITH OUR DEPENDENCE ON THE CELL-LABORATORY OF PLANT AND ANIMAL? In certain special lines, yes; on the whole, most likely an emphatic no. The plants are greater "specialists" than our chemists ever are likely to be. The power they use is the cheapest of all, and the best; it is the glorious sunshine that fills the world so long as man shall live on earth—for he will have to die when the sun shall begin to grow dim. The raw materials of the cell-chemists are also the cheapest of all, namely rain and air. To give plants the best chance to furnish us the highest possible returns, we should work with our hands in field and garden, should plow and plant, harrow and hoe, in order that we may glean and garner for self and others, for home and market. And as in this labor we come in touch with Mother Earth, and draw deeply the air just purified by that beam of power from Father Sun, we become strong in body, and pure in heart, while our soul is filled with Peace and Faith and Hope.

## 91. THE ATOM-WORLD.

1. "Let us remember, please, that the search for the constitution of the world is one of the greatest and noblest problems presented by Nature." This word of GALILEO, taken from his second dialogue on the Systems of the World, we have placed as motto on the front page of this book.

2. The Great World, the MACROCOSMOS of the Ancients, was but the flat earth, surrounded by the sea, and lit up by sun and stars. To Modern Science it is the wonderful, infinite All, in which the earth is but an atom. The mechanical structure of this world Galileo had in mind. He most successfully assisted in the search for its constitution; and was rewarded by persecution, prison and torture.

3. To the searching eye of Science, the atom itself becomes a world; it is the true MICROCOSMOS. The search of its constitution offers no less great and noble a problem than that of macrocosmos. With thermometer and goniometer we have learned to measure the dimensions of the atoms, precisely as astronomers measure the dimensions of the planets with pendulum and theodolite. C. R., T. 76, p. 1594; 1873.

4. The guiding rule in this, our study of microcosmos, is the same that has laid open the constitution of macrocosmos: it is MECHANICS, the mathematical expression of the action of matter through space. This action is independent of the absolute dimensions. The laws of motion apply equally to large and small objects. The planet is but an atom in the world; the silicon atom is half the world in quartz.

5. The science of mechanics was founded by ARCHIMEDES, of Syracuse, twenty-five centuries ago. He established the laws of statics, the science of equilibrium. GALILEO (p. 18) laid the foundations of dynamics, the science of motion. HUYGHENS (p. 20) worked out the laws of rotations and revo-



lutions. From NEWTON'S Principia to LAPLACE'S Celestial Mechanics, this search for the constitution of macrocosmos has been perfected.

6. The beginning of the mechanics of microcosmos may be traced back, even to Galileo himself. About the middle of this century the MECHANICAL CONSTITUTION OF THE GASES seemed to open the field anew. But to the mathematician, the molecule remained merely an elastic ball, while the chemist, dripping with tar, made flat diagrams of complex molecules in utter disregard of the laws of mechanics which he did not care to know.

7. The extreme one-sidedness of German chemistry of the present, which has compelled the government to fill the two principal chemical professorships in Germany with a Russian and a Hollander, is also noted in the SENSATIONAL DECLAMATIONS of one of their most voluminous writers against the great masters of mechanical science, from Newton to Laplace, and his habitual derision of mechanical conceptions in chemical research.

8. We would take no notice of these strange declamations if they were not taken as representing that GERMAN SCIENCE WHICH THE WORLD JUSTLY REVERES. Unmindful of Liebig's equally unfounded authoritative declaration of the impossibility of the true synthesis of genuine organic compounds, young Berthelot performed these syntheses from the elements. In the same manner, the author has continued to establish the constitution of compounds by applying the mechanics of Galileo, Huyghens, Newton and Laplace though these masterminds are denounced by the chemists of the University of Leipzig who writes so much that his thoughts evidently cannot keep up with his pen. See my True Atomic Weights, pp. 42—46; 1894.

9. In the gaseous state, the molecules move freely in space until they hit the walls of the containing vessel or another particle. The flight of the gaseous molecule is free, unre-

strained, like the motion of a projectile or that of a cosmical body. The motion of the gaseous molecules therefore must conform to the established LAWS OF FREE MOTION.

10. The motion of projection or translation is associated with a rotation around one of the permanent axes. For one of these axes, the moment of inertia (mass) is greatest, for the other it is smallest. In continued motion, the body will necessarily come to rotate about the first of these axes, it being the most stable. IN THE GASEOUS STATE THE PARTICLES (MOLECULES) HAVE A MOTION OF TRANSLATION AND ROTATE AROUND THEIR SHORTEST AXIS (i. e., the permanent axis for which the moment of inertia is the greatest).

11. This is the motion of all the cosmical bodies. These motions are best shown by the BOOMERANG. Small card boomerangs allow the instructive and elegant lecture experiment, the two motions being readily seen by all. The experimenter, after a little practice, needs only one boomerang, since it promptly returns to him every time. By attaching balls, chain, hoop, flask with water and colored ether, or water and mercury, to a catgut string, and rapidly TWIRLING the upper end hereof, the rotation will be final around the shorter axis, i. e., the one for which the moment of inertia is greatest.

12. In the SOLID STATE, particles merely oscillate. MELTING, THEY BEGIN TO ROTATE, necessarily AROUND THEIR LONGEST AXIS, being their axis of minimum moment of inertia. Heated high enough, particles will finally be projected from the surface of the liquid, and move freely through space as just described. This MECHANICAL DESCRIPTION OF THE THREE STATES OF AGGREGATION the author has published a quarter of a century ago, and proved it to be true by many deductions, a few of which will now be given.

## 92. PRISMATIC ATOMS AND BOILING.

1. AT THE BOILING POINT, the particles are projected from the liquid in numbers sufficient to BALANCE THE PRESSURE OF THE ATMOSPHERE. At the same pressure, all boiling liquids are necessarily in corresponding condition. We need, to connect them, only to study the relation between pressure and boiling point for any one liquid. C. R., T. 112, p. 998; 1891.

2. To study the FORM OF ATOMS, it is necessary to begin with groups of bodies known to be of the same kind. Such groups we have in the HOMOLOGOUS SERIES of modern organic chemistry. Any given alcohol radical R added to  $-\text{CH}_2.\text{H}$  forms a paraffin; to  $-\text{CH}_2.\text{OH}$  an alcohol; to  $-\text{CO}.\text{H}$  an aldehyde; to  $-\text{CO}.\text{OH}$  an acid; to  $-\text{CH}_2.\text{Cl}$  a chloride, etc., etc. Lecture 87.

3. Let us compare say the HOMOLOGOUS ALCOHOLS, wherein  $\text{R} = \text{C}_m \text{H}_{2m+1}$ . In all these compounds, the active terminal, i. e. that part which can react chemically, is the same, namely  $-\text{CH}_2.\text{OH}$ . It weighs 31. The other part  $\text{R}_m$  may be written  $\text{H} + m (\text{CH}_2)$ . The entire alcohol atom therefore weighs  $32 + 14m$ , where  $m$  is the total number of carbon atoms less one.

4. All the OTHER HOMOLOGOUS SERIES mentioned may be expressed by corresponding formulæ. The paraffins by  $14 + 14m$ . The aldehydes by  $30 + 14m$ . The acids by  $46 + 14m$ . The chlorides by  $48.5 + 14m$ . The bromides by  $93 + 14m$ . The cyanides by  $49 + 14m$ . The amines by  $31 + 14m$ .

5. These substances can be readily changed chemically one into the other—both by changing the radical of  $m$  links  $\text{CH}_2$  and especially by changing the active terminal. It may not be elegant, but it certainly is very correct, to compare the TERMINAL to the head, the RADICAL to the vertebræ of an animal—say a snake. The carbon of the link  $\text{CH}_2$  would represent the vertebra, the two hydrogens the ribs attached thereto.

6. Now all chemists agree that these  $\text{CH}_2$  are joined each way by a simple link or valence. But how is the form of the entire radical: rigid, forming a STRAIGHT LINE, or spiral like a CORKSCREW (86, 4 to 6). Our great German chemists do not know, and therefore declare this question is insoluble, and should not be approached. This admirable system throws odium on anyone who dares to attempt the solution of such a question. They even excuse Berzelius (E. Meyer, History, p. 238, Engl. edition 1891) from having thought such a problem soluble.

7. But reading our GRAND MASTER once again (91, 1) we venture to tread where der Herr Geheimrath has not been. We put the question once more clearly before our eyes: do these m-links of the radical of modern chemists form a rigid, straight line, or do they not.

8. Now, nature has the rather human habit of giving A PLAIN ANSWER TO A PLAIN QUESTION; but, at the same time, she only answers yes or no, and thus gives us no answer at all unless we have taken the trouble to learn how to ask the question. Really, the main difficulty of investigation is to learn to ask the question. That is a mental problem. Our apparatus cannot help us therein.

9. Now TWO LINKS  $\text{CH}_2$  form a straight line; for two points determine such a line. These two points are the centers of gravity; weight 14 each. Let their distance be taken as unity. The moment of inertia of this 2  $\text{CH}_2$  will then be 7 exactly. If the radical forms a straight line, the moment of inertia for 3 links  $\text{CH}_2$  will be 28, for 5 links will be 112, for 7 links 364, for 9 links 812, and so forth. The moment of inertia is the sum of the each weight into the square of its distance from the axis, here the center of gravity or the middle atom.

10. According to 91,10, THE BOILING POINT must be some function of this moment of inertia. If the form of the radical be not straight, the moments of inertia will increase at a much less rapid rate; that popular tetrahedral-corkscrew would show very slowly growing moments of inertia for increasing values of m. On plates 76 and 77 we have copied the

graphical representation of the facts observed (boiling points) and our function of the moments of inertia (simply related to the logarithm of number of carbon atoms). See note on logarithm below.

11. The most NECESSARY DATA have been given in our papers kindly presented by Berthelot to the Academy of Sciences of Paris, and inserted in full in the *Comptes Rendus* of that Academy for 1892. Plates 76 and 77 are simply re-prints from the *Comptes Rendus*. The very curves, however, suffice to give the answer, without entering upon the details of calculation, the leading formulæ for which are inserted on the plates.

12. The answer to the question is complete and decisive. The alcoholic radical  $C_m R_{m+1}$  forms a straight line, so far as the maximum moment of inertia is concerned. ALL SATURATED ALCOHOLIC COMPOUNDS ARE LINEAR, consisting of the rectilinear tail or series of  $CH_2$  links and terminating in the head chemically characterizing the compound as paraffin, acid, chloride, and the like.

---

NOTE.—The log  $n$  of our plates means THE LOGARITHM of the total number  $n$  of carbon atoms of the compound. The actual values, taken from any logarithm table, are given below:

No.	Log.	No.	Log.	No.	Log.	No.	Log.	No.	Log.
.....	.....	10	1.000	20	1.301	30	1.477	40	1.602
1	0.000	11	1.041	21	1.322	31	1.491	41	1.613
2	0.301	12	1.079	22	1.342	32	1.505	42	1.623
3	0.477	13	1.114	23	1.362	33	1.519	43	1.634
4	0.602	14	1.146	24	1.380	34	1.532	44	1.644
5	0.699	15	1.176	25	1.398	35	1.544	45	1.653
6	0.778	16	1.204	26	1.415	36	1.556	46	1.663
7	0.845	17	1.230	27	1.431	37	1.568	47	1.672
8	0.903	18	1.255	28	1.447	38	1.580	48	1.681
9	0.954	19	1.279	29	1.462	39	1.591	49	1.690

Such a table of logarithms can be obtained by noting the consecutive excursions of the pointer of a fine chemical balance during ten to thirty minutes. The number of the oscillation and the corresponding excursion form the logarithmic curve.

. We here have referred to the normal compounds exclusively. We also designedly have taken the weight instead of the mass in the moments of inertia, for obvious reasons.

### 93. ATOM LINKAGE AND FUSING.

1. Having determined the atoms of all alcoholic serials to be rectilinear, so far as the arrangement of the centers of gravity of their links  $\text{CH}_2$  is concerned, the next question is, how are the carbon atoms linked?

2. The rectilinear form established leaves only TWO POSSIBLE MODES OF LINKAGE of the carbon atoms in the alcoholic radical. The carbon atoms may link end-to-end, or face-to-face. That is, since they have some form, say like a watch, they may attract end-to-end, or face-to-face.

3. In the END-TO-END POSITION the carbon atoms could revolve and the hydrogen atoms of  $\text{CH}_2$  might face any direction. The resulting compound would be far from rigid. Yet we have the best of reasons to suppose that element atoms in compound atoms are held rigidly in place, like molecules in a crystal. The end-to-end position is therefore not probable, a-priori.

4. In the FACE-TO-FACE POSITION of the carbon atoms, the structure would be rigid, the hydrogen would alternately turn as the carbon does. The entire atom would be most symmetric as well as rigid. This is a-priori the most probable method of linkage of the carbon atoms in alcoholic, and in fact, in all organic compounds.

5. Let us again submit the question to nature, and first formulate the most probable case. The carbon atoms would occupy positions as the types here printed. The points of

A	C	E	G
B	D	F	H

attraction of atoms A, C, E, etc. would be directed downward towards the corresponding points of B, D, F, etc., directed upwards.

6. IF THE TOTAL NUMBER OF ATOMS OF CARBON BE EVEN, the axis containing the center of gravity of the compound will run exactly midway between the two lines. If the distance be called 2, the moment of inertia will be simply equal to the atomic weight, the distances of all atoms from the axis being unity.

7. BUT IF THE TOTAL NUMBER OF CARBON ATOMS BE ODD, the result will be entirely different. Suppose we have three atoms only. In that case the center of gravity evidently is much nearer the two atoms A and C than the single atom B. In fact, everyone understands the space is divided as one to two. The distance from the geometrical middle to the real axis is one-third unit.

8. If the total number be five atoms of carbon, the four will balance exactly. But the fifth will evidently draw the center of gravity one-fifth unit up from the middle line. That is, the permanent axis of rotation, which passes through the center of gravity of the system, lies one-fifth unit of distance away from the geometrical axis or middle line. For seven atoms it will be one-seventh, and so forth.

9. Now it is a simple principle in mechanics, that the moment of inertia of any body, or system of bodies, is smallest for the axis passing through the center of gravity. For ANY AXIS at any distance PARALLEL to the first axis, the moment is greater by a quantity proportional to the SQUARE of this distance.

10. Consequently, the moment of inertia for the alcoholic serial compounds considered, in reference to the permanent axis parallel to the length of the system, increases proportional to the total atomic weight of the entire system; but for compounds of an ODD NUMBER N OF CARBON ATOMS the moment of inertia is diminished by a quantity proportional to the square of one-nth of the total number of carbon atoms.

11. But this moment of inertia determines the fusing point of compounds (91, 12). Hence the FUSING POINT OF ALCOHOLIC SERIALS IS SMALLER FOR COMPOUNDS HAVING AN ODD NUMBER OF CARBON ATOMS, THAN FOR THOSE HAVING AN EVEN NUMBER of carbon atoms; the difference, being inversely proportional to the square of the number of carbon atoms, will rapidly diminish as  $n$  increases and vanishes when  $n$  becomes sufficiently large.

12. But this is precisely the case for the paraffins, the fusing points for which have been presented in curves D and C of Fig. 6, page plate 74, according to the observations of Krafft. See for fuller data, Comptes Rendus, May 19, August 17, and November 22, 1891. HENCE THE CARBON ATOMS ARE JOINED FACE-TO-FACE in the organic compounds. No such marvelous and hitherto utterly inexplicable differences could occur in the end-to-end position between compounds containing even and odd numbers of carbon atoms.

THE FATTY ACIDS show the same differences in a most striking manner. These remarkable differences have puzzled modern chemists greatly. The deductions given make the determinations of the fusing points an experimentum crucis for the linkage of the carbon atoms, as here shown.

For the fatty acids, the fusing points  $F$  and the total number  $n$  of carbon atoms are given in the following little table. It will be noted that the melting point of the odd-numbered acid is from 3 to 2 below that of the preceding even-numbered acid, while the next even-numbered acid is from 20 to 6 degrees higher:

$n$	$F$	$n$	$F$	$n$	$F$
8	16.0	14	54	20	75
9	12	15	51	21	72
10	31.4	16	62	22	78
11	28	17	60	23	.....
12	43.6	18	69	24	80.5
13	40.5	19	66.5	25	77



## 94. ATOMIC VOLUME.

1. The atomic volume of any compound in the solid or liquid state is the volume, in cubic centimeters, occupied by one gramme-atom of the substance. THE ATOMIC VOLUME OF WATER IS 18; for each cubic centimeter of water weighs one gramme, and the atomic weight of water is 18.

2. The specific gravity of any substance being the weight, in grammes, of one cubic centimeter of that substance (2, 11), it follows that THE ATOMIC VOLUME IS OBTAINED BY DIVIDING THE SPECIFIC GRAVITY OF THE SUBSTANCE INTO ITS ATOMIC WEIGHT. For water, G is 1, the atomic weight 18; hence the atomic volume is 18 cc per gramme-atom.

3. Plate p. 394 gives the specific gravity for the liquid PARAFFINS  $C_n H_{2n \times 2}$  from  $n = 5$  to  $n = 35$ . The points connected by dots form the SPECIFIC GRAVITY CURVE of this homologous series. The curve first rises rapidly, then turns, and from  $n = 16$  changes but very little. That is, the specific gravity of the higher paraffins is almost constant. They could not be distinguished by their gravity.

4. Figure 5 on the same plate represents the ATOMIC (or molecular) VOLUME of these paraffins. It will be noticed that this curve is practically a straight line. Only for the lower compounds (from 5 to 10) is the volume slightly in excess of the corresponding points on the straight line. For 22 the volume is 400; hence practically 18 for each link  $CH_2$ .

5. The higher paraffin atoms accordingly occupy a PRISMATIC SPACE equal to as many times the atomic volume of water as the paraffin contains carbon atoms or links  $CH_2$ . The very deviation for the lower members, the author has shown to be due to the two terminal hydrogen atoms, the influence of which rapidly becomes insensible with the increase of the number of carbon atoms. C. R., T. 113, p. 37, Equat. 22; 1891.

6. The equality of the atomic VOLUME OF EACH LINK  $\text{CH}_2$  in paraffins with that of water has also been recognized by the author fully thirty years ago. The atomic volume of alcohols and acids being approximately one water volume in excess of that of the corresponding paraffin, shows that the terminals of  $-\text{CH}_2 \text{ OH}$  in alcohols and of  $-\text{CO. OH}$  in acids make the hydroxyl  $\text{OH}$  nearly equal to the link  $\text{CH}_2$ .

7. Accordingly, all these homologous series may be looked upon as forming PRISMATIC ATOMS of the same cross-section (very nearly), and differing only in length. The cross-section evidently equals that of the water atom, which becomes a convenient unit. The cross-section we have called ATOMARE, the length ATOMETER (Atomechanics, 1867). The atometer of a paraffin is  $n$ , that of an acid or alcohol  $n + 1$ , if  $n$  represents the total number of carbon atoms, arranged in a single straight line (normal).

8. THE ATOMIC VOLUME of homologous series MAY BE CALCULATED by two methods, namely, the statical and the dynamical method (C. R., T. 113, p. 36; 1891). In the STATICAL METHOD, the volume of the atomic prism is determined from its section, which is constant in the same and correlated series, and its length. The case of the paraffin series is given as example.

9. In the more general and more interesting DYNAMICAL METHOD, the rotary motion of atoms around their longer axis is made use of; it is, of course, applicable to liquids only. In this case the atom-volume is a cylinder of revolution, the base of which is the circle described in the rotation, while the length is that of the axis itself.

10. This method has been applied to OVER SIXTY ETHERS for which the necessary data are known. The results of the calculations agree admirably with the observations. The cross section of these ethers is one-third larger than that of the paraffins. This is the expression of the fact that the ethers contain the link  $\text{O}$ , connecting the radicals, projecting

above the  $\text{CH}_2$  one-third its height. See C. R., T. 113, p. 37; 1891.

11. One of the most remarkable confirmations of this prismatic or cylindrical form of the atoms of serial organic compounds has been found in the laws of the MAGNETIC ROTATION of polarized light produced in liquids. In looking over recent work of W. H. PERKIN, who has furnished most elaborate and extensive observations in this field, numerous further confirmations are noticed. C. R., T. 113, p. 500; 1891.

12. The exposition of this subject of atomic volume in leading MODERN GERMAN WORKS is really astonishing. German scientists used to be proud to know work done in other countries as well as that done within the limits of the old Fatherland. At present, this has become merely a historic reminiscence. In Ostwald's Biggest Book on Chemistry, the crude ideas of Kopp are still law, and the search for the fixed atomic volume of each element atom is lustily continued as it was begun fifty years ago.

## 95. ISOMERIC ATOMS.

1. Having established, by induction, the structure of alcoholic compounds, we may now make use of the easier METHOD OF DEDUCTION to establish some of the principal laws governing the physical properties of the compounds.

2. The first compounds which invite our attention are the Isomerics (84). They result from ISOMERIC ATOMS, namely different structures built up from the same number of atoms of the same elements, in accordance with the laws of linkage.

3. Thus the paraffin NORMAL PENTANE  $\text{C}_5\text{H}_{12}$ , boils at about 38 degrees. It is normal, having its five links all in one straight line. Chemical treatment has failed to remove shorter links from the same. It has no lateral branches.

4. But the same five carbon atoms might be so linked as to have one or more lateral branches. If it has only one  $\text{CH}_2$  lateral, and near the terminal, it is called ISO-PENTANE. This hydrocarbon boils at 30 degrees, fully 8 degrees lower than normal pentane.

5. Finally four lateral branches  $\text{CH}_3$  might be bound to one central carbon, from the same 5 carbon and 12 hydrogen atoms. This isomeric compound is called TETRA-METHYL METHANE. It boils at 9.5, about 30 degrees below the normal pentane. It is liquid at common temperatures, but fuses at  $-20$ .

6. Now it needs only a moment's consideration to understand these REMARKABLE DIFFERENCES. As the carbons are placed in the lateral branches, their distances from the center become less; consequently, the moment of inertia, depending on the square of these distances, must greatly diminish. Hence the boiling point must be lowered correspondingly (92, 10 - 12). See Plate, page 78.

7. For example, the MAXIMAL MOMENT OF INERTIA (omitting single terminal hydrogens) of normal pentane is  $10 \text{ CH}_2 = 140$ , while that of tetra-methyl methane is only  $4 \text{ CH}_2 = 56$ , or about one-third. In the first we have two links  $\text{CH}_2$  at the distance two, giving a moment of inertia 4.  $\text{CH}_2$  each. In the final isomeric, these two links are at the unit of distance, and only give the moment 1.  $\text{CH}_2$  each. This fully explains the changes in boiling points.

8. As links are made lateral, the MINIMAL MOMENT OF INERTIA for the main or larger axis will be greatly increased with their increased distance from that axis. Accordingly, tetra-methyl methane melts at a temperature at which normal paraffins of even twice that number of carbon atoms remain liquid.

9. In the same manner, the ISOMERIC ALCOHOLS containing 4 carbon atoms are all liquids except the trimethyl carbinol, having three lateral arms  $\text{CH}_3$ . It forms rhombic crystals melting at 28 degrees. In this atom, the longer axis is

$\text{CH}_3\text{-CH-OH}$  and to the carbon of the middle the two  $\text{CH}_3$  are linked, greatly increasing the moment of inertia for this axis.

10. MY FIRST PUBLICATION on this subject appears in the Proceedings of the American Association for the Advancement of Science for 1868 (Chicago meeting). Complete mathematical formulæ were sent in my *Beiträge* to the German Chemical Society at Berlin in 1872, of which I was a member. Several papers of mine were presented by Berthelot to the Academy of Sciences of Paris and published in the *Comptes Rendus* from 1873 on. See T. 113, p. 798; 1891.

11. DR. ALEXANDER NAUMANN, Professor of Chemistry at the University of Giessen, Germany, was one of the paid writers for the *Jahresbericht*. He misrepresented and condemned my paper of 1868 on this subject in the *Jahresbericht*. In 1873 he discovered my law over again as his own, and his discovery was promptly published in the *Berichte* of the German Chemical Society of Berlin. In all German chemical publications this law is credited to Naumann, even in W. Markwald's "*Beziehungen*" which were crowned with a prize by the University of Berlin, in 1888, under the auspices of Geheimrath A. W. Hofmann.

Thus the young German writers on the *Jahresbericht* make their discoveries, and no protest is raised by German scientists. Until that is done they must be considered as endorsers of that practice. I demanded my name erased from the list of members of the German Chemical Society (March 27, 1874). See my *Beiträge*, Leipzig, 1892.

12. It will readily be seen that the structure now established fully accounts for the RIGHT- AND LEFT-HANDED (geometric) ISOMERICS, and therefore determines the character of rotary polarization. A simple construction of the stereographic formulæ of the tartaric acids will exemplify this. Compare figures 1, 2, 3, page 394. The face-to-face linkage of carbon is most essential also in this matter. The interesting hexachlorides of Benzol, due to Friedel, obtain their fullest importance in this construction.

## 96. ATOMIC ROTATIONS.

1. The reality of ATOMIC ROTATIONS in the liquid and gaseous states is also most conclusively demonstrated by the results obtained as specific heat (39 and 40) of substances in these states. We shall first consider the specific heat of gases.

2. The specific heat of a gramme-molecule of any gas or vapor is the number of gramme-degrees of heat required to raise the temperature thereof one degree (centigrade). If the volume be kept constant, the gas does no external work; if the PRESSURE BE KEPT CONSTANT, the gas expands and thus does external work. According to G. Schmidt, this EXTERNAL WORK amounts to 2 calories (gramme degrees).

3. While the temperature changes, the particles may also act upon one another, and thus do some INTERNAL WORK. For perfect gases, like oxygen and hydrogen, this amount is not measureable, but for vapors it may be of appreciable magnitude. We will represent it by the symbol  $w$ .

4. THE ACTUAL ENERGY OF MOTION is represented in the vibration of the atoms, the motion of translation and of rotation of the entire molecule. The first depends evidently upon the number of atoms in the molecule. Naumann considers it equal to as many calories as the molecule has atoms; say  $n$ . The motion of translation represents 3 gramme degrees, according to Clausius.

5. THE MOTION OF ROTATION requires an amount of energy proportional to the moment of inertia,  $I$  of the molecule; hence we can call it  $k I$  calories per gramme molecule (Comptes Rendus, T. 76, p. 1358; 1873, and Principles of Chemistry, 1874; p. 118). For many gaseous alcoholic compounds we have found  $k$  one-eighth of a calory.

6. Thus the total specific heat (under constant pressure) of a gramme molecule of any GAS OR VAPOR becomes

$$S = 5 + w + n + k I$$

For LIQUIDS, the same formula will obtain, except that the external work is insignificant for a degree, and that the moment of inertia  $i$  is taken for the longer axis. Hence

$$S' = 3 + w + n + k i$$

7. The gases and vapors considered by me in 1873 agree excellently with this formula  $S$  and therefore PROVE THE ROTATION OF THE MOLECULES of gases and vapors around that permanent axis for which the moment of inertia is a maximum. We shall come back to this subject in the next lecture.

8. THE ETHERS OF THE FATTY ACIDS have been found to be truly prismatic bodies (94, 10). Their moment of inertia is accordingly directly proportional to their length, the cross-section being the same throughout each one and for all. Hence the specific heat per unit of weight must be the same for all these ethers (C. R., T. 113, p. 469; 1891).

9. R. SCHIFF has found this specific heat for all equal to 0.442; he has studied 27 of these ethers (l. c.) Ostwald declared this result to be "most unexpected." But we see that it is simply the expression of the equal cross-section of all these prismatic bodies. THE DETERMINATION OF SCHIFF therefore are a direct demonstration of the rotation of the molecules of these liquids around their longer axis.

10. FOR SOLIDS, the term containing the moment of inertia disappears, because the molecules of solids do not rotate. The expression in 6 is reduced to

$$S' = 3 + w + n$$

where the internal work  $w$  now becomes very considerable. These results, being old and long established, need not be considered here.

11. The specific heat of the SOLID ELEMENTS are equal, namely nearly 6; hence the internal work is about 3. Berthelot has first (1873) pointed out that elements herein radically differ from all compound matter. I have shown (1892;

C. R., July 25) this to be due to the fact that the elementary atoms oscillate as a unit, or that THEIR COMPONENT PARTS ARE INVARIABLY FIXED, not mutually movable.

12. Recently Berthelot (C. R. Jan. 18, 1897) has carefully compared the specific heat of the elementary gases and of ARGON AND HELIUM. He thinks it probable that they vary as 1 : 2 : 4 according as the molecule contains 1, 2, 4 atoms. But he has overlooked the atomic rotations.

The entire difference between 6,8 (chlorine) and 4,8 (oxygen) corresponds to AN INCREASE OF ONLY 16 PER CENT. IN THE DISTANCE between the two atoms of chlorine in its molecule over that of the oxygen atoms. The latter does not dissociate, the former does yield to heat.

## 97. ATOMIC LIBRATION.

1. When Galileo had directed his telescope upon the face of the moon, he recognized slight changes. It seemed that the moon's face turned a little, like the beam of a balance. He accordingly called the phenomenon the LIBRATION OF THE MOON. It has occupied observers and mathematicians for over a century.

2. The real home of the balance is the chemical laboratory. THE TRUE LIBRATION IS THAT OF THE ATOMS. It is of more decided importance in molecular mechanics than that of the moon in cosmical mechanics. It is of infinitely greater extent, also. Such "titubazione" in macrocosmos would be destruction.

3. Are the PHENOMENA OF ATOMIC LIBRATION occult and hard to see? Oh, no! They are so manifest that they stand boldly out from the tabulated data of boiling points, of fusing points, circular polarization, magnetic rotation, and others.



4. What phenomena are here referred to as due to atomic librations? The whole world of TAR-DERIVATIVES is dripping full of them! There is benzol, crystallizing at about the same temperature as does water. Put one chlorine in the place of one of its hydrogen, and down goes the fusing point half-a-hundred degrees. Replace still another atom, and the fusing points jumps up a hundred degrees. Thus it keeps alternating up and down, while the benzol atom is being gradually loaded with chlorine instead of with hydrogen. Here you have the continuity of nature in the chemical process, and rank discontinuity in the physical result. The chemist moves by continuous steps—and nature jumps like a see-saw!

5. And in truth, IT IS A SEE-SAW. You balance a plank nicely. A little boy jumps on—down goes his end of the plank. The boy's playmate manages to get onto the plank and walks to the other end—down that goes, carrying up the first one. Here we have the libration of a plank, produced by two little imps full of fun and mischief. Atomic libration is mechanically produced in the same manner.

6. Here is a benzol atom (Plate page 395); THE FAMOUS BENZOL RING AS IT IS IN REALITY, shown in ground plan or horizontal projection, in accordance with our established atom-linkage. Suppose the hydrogen atom place 1 be exchanged against an atom of bromine. What will happen?

7. The total benzol weighs 78. The single bromine substitution adds 79 thereto and doubles it. The CENTER OF GRAVITY moves from the center of the ring half way towards place 1. The effect on the moment of inertia for the vertical axis is easily calculated—determining the boiling point. For the axis parallel to the paper, determining the fusing point, the case is a little more complicated.

8. The old axis—for benzol itself—was parallel to the plane of the projection, and passed through the center of the ring, that being the center of gravity. THE NEW AXIS, for the

mono-bromide, FORMS QUITE AN ANGLE with that plane, roughly passing through the bromine atom and that center of the ring. Thus the added weight of bromine at distance zero adds almost nothing to the moment of inertia, which has been greatly reduced by the displacement of the center of gravity.

9. But now add another atom of bromine where it will produce THE GREATEST MECHANICAL EFFECT, that is IN PARA-POSITION, at 4. Since the H or Br at 1 is in the plane of carbons, 2, 4, 6 and the H or Br at 4 in plane with carbons 1, 3, 5, the two bromine in para-position (1, 4) balance, restore the center of gravity to the center of the ring. Hence we have their full distance effected in the moment of inertia, which goes up about twice as much as the first depressed it. In the tetra-bromide (1, 4; 2, 5) we have two para-positions; hence double rise of melting point. In hexa bromide we have three para-positions (1, 4; 2, 5; 3, 6) and hence threefold rise. The change of inclination becomes less as the total weight increases. Hence the rise in fusing point for the second and third para—addition is greater than for the first.

In the tri-bromide (1, 4; 2) we have the para position (1, 4) added to 2. So also the penta-bromide is one added to the di-para (1, 4; 2, 5). The diagram for chlorides shows from Benzol the fusing points of the para-compounds at B, D, F (mono-, di-, tri-para) and the depressed monochlorid at A, raised by two paras (mono-, di-) to C and E. Page 395.

This is the simplest case of atomic libration. Without using a mathematical formula I trust THE PROBLEM IS CLEARLY STATED AND ITS SOLUTION FULLY INDICATED. The plate (p. 395) shows that the case is general, applying to all chloroids. For radicals, the case will be modified by their open structure, as shown long ago. See C. R., T. 115, p. 177; 1892.

10. It will be understood that these LIBRATIONS AFFECT NEARLY ALL PROPERTIES. Thus the para-compound necessarily occupies the greatest volume—as Feitler has found experimentally. Our modern journals are full of facts—for it

is facts, you know, new observations, "eigene Bestimmungen," that our Geheimräthe want—for such things can be manufactured by the students, and be published "in stattlichen Bänden."

11. The state of my health has not allowed me thus far to publish either of the volumes planned to succeed my True Atomic Weights. The solution here given is, however, broad and complete. ANYONE UNDERSTANDING MECHANICS CAN PUT THE SOLUTION INTO EQUATIONS. It is a simple matter of detail. I will only add, that the case of "odd and even compounds" of alcoholics (Lect. 93) is really also involving an inclination of the axis, especially where the terminal is heavy, and the number of carbons low, as in formic and acetic acids. One of the most interesting cases of atomic libration is presented in the THREE CHLORACETIC ACIDS; however, the calculations are rather intricate.

12. The Ring-Form of Benzol has been demonstrated by my formulæ in 1874 (Principles, p. 120; also C. R., T. 80, p. 47; 1875). The above formula (Lect. 96, 6) for benzol vapors gives  $I = 70$ , since  $S = 29.26$  observed, and  $n = 12$ , the internal work being taken at 3.5 as for alcoholics. If this be less, the moment  $I$  will be correspondingly greater.

But for the six CH forming a straight line, the moment would be at least 227. This is entirely at variance with the above value due to the specific heat. If the center of gravity of the six carbons be at a distance  $r$  and those of hydrogen at  $r$ , the moment of inertia will be  $6 \cdot [C \cdot r^2 + H \cdot r^2]$ . Taking, as first approximation  $r_c = r_h$  we find  $r = 0.95$ . This is very nearly the value 1.00 of our construction, p. 395.

---

NOTE.—In looking through Perkin's determinations of magnet rotations in the closing number for 1896 of the bulky Zeitschrift, I notice a multitude of the plainest confirmations of these principles. The  $\alpha$  much greater than  $\beta$  (p. 633) because ortho have new weights nearest and on opposite sides of the central plane—producing maximal torsion. So  $\alpha$  naphthols greater than  $\beta$ , p. 635.

## 98. ATOMIC CRYSTALS.

1. The old Teutons and Scandinavians believed that "Cobolde" and "Nisser" inhabit the caves of the earth, gather metals and skillfully work them into ornaments and weapons which they bestow as gifts on their favorite among women and men. But if man surprises them, these dwarfs suddenly assume the form of beautiful crystals, which therefore are called QUARTZ (dwarf). See Dedication, 3rd section.

2. The magnificent quartzes of the Alps were well known to the Romans, for Pliny speaks of them at length (15, 2). They supposed them to arise from celestial vapors and purest snow; but WHY THEY GROW SIX-SIDED, Pliny deems it hard to tell. *Quare sexangulis nascitur lateribus non-facile ratio inveniri potest* (Hist. Nat. 37, 9).

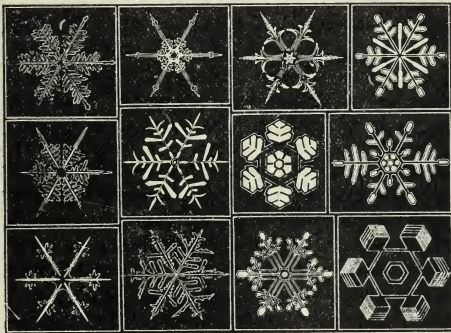
3. From celestial vapors forms purest snow indeed—and that SNOW HAS ALSO THE SIX-SIDED FORM. Every-one in northern countries can see these star-like forms if he will but look at the snow lodging on his coat on a dry, cool winter day while snow is falling. A simple magnifier will reveal most of the beauties of these snow-stars.

4. Though so common and abundant an object, the real six-sided form of the snow-star was not noticed before Kepler, who described them 1611 in a special publication of 24 pages quarto: *DE NIVE SEXANGULA*. How did it happen that the astronomer Kepler saw what all others had overlooked?

5. Kepler's mind was filled with the PYTHAGOREAN AND PLATONIC IDEAS of geometrical and numerical harmonies in Nature. He had published (1596) his *Mysterium Cosmographicum*, in which the five regular bodies are made to determine the dimensions of the planetary system. In 1619 he finally completed his search for the great laws of the solar world, as published in his *Harmonices Mundi*.

6. No wonder that such a man would notice with delight the beautiful and regular forms of the six-sided snow-stars! He even went further and asked: *Cur antem sexangula?* This question has remained until I showed in my Programme (1867) WHY THE SNOW-STAR IS SIX-SIDED. In the Scientific American for April 18, 1868, this question is fully answered in popular form.

7. Water is represented by the formula  $H_2O$ . Every atom of water consists of three distinct particles, namely, two of hydrogen and one of oxygen. But three equal material points can only remain in stable equilibrium if they are equidistant, that is, FORM AN EQUILATERAL TRIANGLE. These triangles, aggregating in parallel positions, form a regular six-sided star. This is the actual form of the snow-star. See drawings of Glaisher (below) and the beautiful microphotographs (p. 53) published by Dr. Hellmann (Berlin, 1893).



8. The formula of quartz is  $SiO_2$ . Its crystal form must, therefore, also be hexagonal. So it is. Even its rotary polarization is accounted for in this way. See my communication UEBER DEN BAU DES QUARZES to the Academy of Sciences of Vienna, presented by Haidinger (Sitzungsberichte, I Abth., Bd. 61; 1870).

9. This explanation must be supplemented by the determination of THE THIRD DIMENSION or axis. When a liquid crystallizes, its molecules cease to rotate; they aggregate according to the quadratic form inscribed in the cylinder of rotation. See half page (34) from my *Programme der Atommechanik* 1867, reproduced on page 399 in two-thirds its original dimensions.

10. This shows the cause of dimorphism (21, 7). At the same time, the constituent atoms, not being equal in the compound or crystal-atom, the exact dimensions will be subject to small perturbations depending on the actual atomic weights. These MOLECULAR PERTUBATIONS have been determined in my paper read at the Salem meeting (1869) before the American Association for the Advancement of Science (Proceedings, pp. 100-112).

11. Even the case of TRIMORPHISM of titanite oxide has been fully considered in 1867 (*Programme* pp. 32-33). It may be added, that Tridymite is the ice-form of silica, as already published in a circular of August 1868. A very concise, connected exposition of this entire subject is given in my *PRINCIPLES OF PURE CRYSTALLOGRAPHY*, 1871; 44 pp.

12. THE DETERMINATION OF THE CRYSTAL-AXES from the measurement of the crystal angles is shown in the case of the two forms of sulphur on page 69. It is evident that the inclination  $Pq$  gives the ratio of the axes  $B$  and  $C$ , while the plane angle on  $P$  gives the ratio of the axes  $A$  and  $B$  in native sulphur or sulphur crystallizing from its solution in bisulphide. Lect. 21.

13. The simple case of sulphur (p. 69) also shows how THE SECONDARY FACES  $P$ ,  $q$ , are related to the primary octahedron  $O$ , the dimensions of which are taken as the axes  $A$ ,  $B$ ,  $C$ . For quartz and calcite, a few of the very numerous secondary faces are shown on plate 65. The plates pp. 56 to 64 give reduced copies of eighteen of the excellent plates of v. Kokscharow showing secondary faces of leading crystallized

minerals. These plates are constantly referred to in crystal description and in our crystal practicum.

14. The true ORIGIN OF SECONDARY FACES was discovered by the crystalloclast, Haüy (see p. 55). A fine calcite prism (Fig. 1) inadvertently dropping from his hands, he found that its cleavage gradually lead to the fundamental rhombohedron of 105 degrees, see Figures 2 to 5; compare Lect. 11, 12. From the scalenohedron he obtained the same cleavage form (Figures 6, 7). So he did from all other calcite forms (Fig. 8). Compare calcite, p. 65.

15. Accordingly, Haüy considered a minute cleavage rhombohedron THE CRYSTAL-MOLECULE of calcite. By Figure 17 (p. 55) he shows how the scalenohedron is built up from such molecules. On page 392 we copy his synthesis of the dodecahedron and the pyritohedron from minute cubes. In a like manner, all the varied tesseral forms (pages 58, 59) can be built up from minute cubes.

16. THE MARKINGS OF THE SURFACES often show the reality of this mode of growth of the crystals. The striations of the cubes of pyrite mark the lines of growth of the pyritohedron (9, 12). The horizontal striæ of the prismatic faces of quartz (Lect. 10, 6 and plate 65) mark the edge  $z$  r, and really the disc of  $\text{Si O}_2$  atoms. It is in French works that nature's own way, recorded by Haüy, is still properly presented. See Friedel, *Minéralogie*, Paris, 1893.

17. It is only these natural forms and their AXIAL EQUIVALENTS OF WEISS, of Beriin, that are fit for use in the study of the origin of crystal forms and dimensions. It gives me sincere pleasure to see that the author of the best crystallochemical mannual, Professor C. F. Rammelsberg of the University of Berlin, emphatically expresses the same views and conforms thereto in his admirable *Handbuch* (First edit., 1855 and 1857; second, 1881, 1882).

18. This mere glance at the origin of the wondrous crystal forms may suitably be closed by a reference to my statistical

investigations of the relative FREQUENCY OF THE HIGHER FORMS OF SYMMETRY, presented for me to the Academy of Sciences by the profound Haidinger (*Sitzungsberichte*, Abth. I, Bd. 62; 1870). I find the higher forms of symmetry excessively predominant in nature. The probability of a tesseral form is many million times that of any given triclinic form.

19. A few of the points established by me almost thirty years ago and published in the *Sitzungsberichte* of the Academy of Sciences, of Vienna, have recently found their way into the great Leipzig Organ of Ostwald—of course as a new discovery (Retgers).

20. This reminds me that James D. Dana, after having studied my paper, which was for months (1867) in his possession, made a complete scientific somersault in the July and September numbers of his *Journal* for 1867. Since my *Atomechanik* had appeared in June, he was compelled to admit priority of publication, but brazenly claimed “independent thought in independent minds.” It is remarkable that the mind of Dana did not reach the third dimension, but only my law of symmetry in the one plane. It so happened that this part was the only one in his hands. Hence his independent editorial mind could not proceed for lack of copy. Servility bows to position and power; but honor and truth will prevail in the end.

---

### SUPPLEMENT TO ATLAS.

But few of the instruments intended to be shown were left in each group, which still shows some overlapping and thus may call for verbal explanation. Space demands limitation to the most remarkable case, the compound blowpipe on page 388. The Kipp produces the oxygen (p. 170). This is probably the simplest possible manner of showing the magnificent shower of sparks from burning watch springs and the dropping of molten platinum from a good sized wire. Instead of illuminating gas here used, another Kipp will furnish the hydrogen gas, and complete the outfit. The compound jet must have fine perforations and be nicely adjustable. I use a jet taken from a calcium light outfit for compound gases.



## 99. ATOMIC WEIGHT.

1. The smallest particle of matter entering into chemical combination with any other such particle, is called a **CHEMICAL ATOM**. Its weight is called the atomic weight of the substance concerned, expressed in any convenient unit of weight. The methods used and results obtained in the determination of the atomic weights of the elements have been given (Lect. 40).

2. Dalton introduced this idea into chemistry, about a century ago (Lect. 40, Note). His **TABLE OF ATOMIC WEIGHTS** was small, but remarkably good for a first attempt. Both his law of combination and the real values of the atomic weights received their experimental demonstration at the hands of that great chemist who for a life time was without a peer—Berzelius, of Sweden (p. 22).

3. **BERZELIUS** devised the most exact methods of analysis and applied these methods during forty years to the determination of the atomic weights of the elements, several of which he himself discovered (Se, Si, Th, Va). The first connected exposition of his results are given in his *Essay sur la théorie des proportions chimiques*, Paris, 1819. This work also forms part of his elements of chemistry, which for a quarter of a century remained the textbook of the chemical world.

4. In 1840, **DUMAS** (p. 25) began his fundamental work on atomic weights, determining that of carbon and of hydrogen in reference to oxygen (Lect. 31, 3—8). The atomic weight of oxygen being taken at 16, that of hydrogen is 1, that of carbon (diamond) is 12, exactly. His work has unjustly been drawn in question. He also made admirable determinations on silver in the dry way (21, 10).

5. **STAS** (p. 33) was permitted to assist Dumas in his combustion of the diamond. He made many determinations at Brussels, on silver and its nitrate, sulphate and sulphide, and especially in the wet way with chlorine, bromine and

iodine. He knew to surround his results with a halo of excessive accuracy in the form of mathematical calculations; but since his atomic weights vary with the amount operated upon, the accuracy assumed is not real.

6. Since Hofmann of Berlin made chemical patents so popular among German chemists, the latter have added scarcely anything to this field of science, beyond the most extravagant endorsement of the perfection and accuracy of the results of Stas. To question the absolute reliability of the values of Stas—and of his philosophical conclusions—is generally taken in the Fatherland as a sign of inferiority.

7. As a glaring specimen, I have printed a complete translation of the ENDORSEMENT OF STAS by the editor of the *Jahresbericht* and his thirteen paid aids. See my *True Atomic Weights*, p. 37—38; 1894. The absurdity of the style and language of this document, and the evident lack of understanding of the subject, makes it one of the most characteristic documents of modern chemistry.

8. STAS AND HIS SCHOOL BELIEVE they have demonstrated that THE ATOMIC WEIGHTS OF THE ELEMENTS ARE NOT EXACT MULTIPLES of half the atomic weight of hydrogen. Stas and his school therefore consider it experimentally demonstrated that the chemical elements cannot be taken as compounds of one single material or substance.

9. In the work of mine just referred to (256 pp. with many plates) I have critically examined both the chemical work and the mathematical reductions thereof. My result has been that BOTH THE CHEMICAL WORK AND THE MATHEMATICAL REDUCTIONS THEREOF are entirely unworthy of the consideration in which they are held, a consideration due to lack of real critical study.

10. The chemical work of Stas does not comply with the first condition of all chemical analysis, that its results must be independent of the amount operated upon. IT IS ABSURD to suppose that the atomic weight of silver can vary according as it is part of 10 grammes, 100 grammes or 400 grammes.

The Stasians say, these differences are small; true, but they are of the very magnitude on which the conclusion they draw depends for support. See plate, page 79.

11. THE MATHEMATICAL REDUCTIONS of the Stasian school (made by Ostwald, Karl Seubert, Lothar Meyer of Germany, Thomsen of Denmark, Sebelien of Norway, Van der Plaats of Holland, F. W. Clarke of the United States) is something really astonishing. It would be decidedly amusing, if the errors which this school supports by its spurious science were not so serious in their consequences.

12. I do not need to enter upon details in this place. I may refer to my book, THE TRUE ATOMIC WEIGHTS of the Chemical Elements and the Unity of Matter, St. Louis, Mo., U. S., 1894. The main topics of this work were first published in the *Comptes Rendus* of the Academy of Sciences of Paris, in volumes 115 to 118 (1892—1894), thanks to the kindness of Berthelot.

13. Not only the entire method of reduction used at present is faulty, but our chemists employ a sort of FLOATING BUOY INSTEAD OF FIXED, IMMOVABLE MARK. It is incredible, but true. Hence they never can tell where they are. See *Comptes Rendus*, T. 116, p. 695; 1893. The proper method to be used is also presented in that article.

14. Furthermore, it is necessary to adopt the most permanent and definite element as the STANDARD OF MATTER for the system of atomic weights. THE DIAMOND is the only elementary substance that can be used. For details see *Comptes Rendus*, T. 117, p. 1075; 1893. Also *True Atomic Weights*, p. 174. The system of weights so resulting is represented on page 398.

15. Publications of the Smithsonian Institution and the position of our government chemists are strongly Stasian. So is the work of the young chemist at Harvard and that of Professor Morley, whose work for years has been assisted by funds of the American Association for the Advancement of Science. They ought to be satisfied with the overwhelming

majority and not suppress an individual dissenter. It is just barely possible that nature alone decides.

16. While our Stasian's rejoice in the results of Morley and applaud his presidential address at Buffalo (August, 1896), we hear from Leduc of Paris (C. R., T. 123, p. 807; 1896) that the weight, in grammes, of a litre of oxygen is 1.4293, of nitrogen 1.2507. Now one-sixteenth of the first is 0.08933 and one-fourteenth of the latter is 0.089335. THESE ATOMIC WEIGHTS ARE CERTAINLY COMMENSURABLE.

17. The value of this quotient should agree with the weight of a liter of hydrogen gas, see page 196. THE WEIGHINGS OF HYDROGEN made are 0.0898 or about half a milligramme in excess per liter. Of course, our experimenters, especially Professor Morley, could not commit such an error. His hydrogen, he says, was pure. And yet, it is a fact, that for a century our experimenters overlooked THAT LITTLE ONE PER CENT. OF ARGON in the air, and relied on the false weight of nitrogen until Lord Rayleigh discovered this source of error!

18. I cannot close this lecture without mentioning two of our younger American chemists working in this line—Professor RICHARDS at Harvard, and Professor EDGAR F. SMITH at Philadelphia. The former—a dyed in the wool Stasian—recently found Mg 24.5, by starting with something he does not know what, and ending with something he knows as well. This result represents an error of over two per hundred on the value Mg 24. I am not competing in this work; but my gasometric work proves that the fine work done at Harvard is altogether too fine. A little error of two per cent. in the atomic weight of an element used in many quantitative determinations (phosphate, etc.) is really a tangible and substantial achievement for Old Harvard.

In the Laboratory of the University of Pennsylvania, atomic weight determinations are also made. I have been delighted with the evidence that Professor Smith deems is as necessary to weigh known substances as BERZELIUS did.

## 100. ALCHEMY AND ELEMENT.

1. The researches of Berthelot in THE EARLY HISTORY OF CHEMISTRY are as important as they have been extended (see pages 42, 43). An outline of his labors we have in the elegant edition (Paris, 1885) of his fascinating work: *Les Origines de l'Alchimie*. His later works have been on a large scale every way.

2. Berthelot has strongly accentuated the kinship of thought between the alchemist and the modern chemist in reference to THE CONSTITUTION OF MATTER. What sounded strange forty years ago to prominent men in letters of mine, and thirty years ago in my Programme (1867) is now tacitly admitted.

3. Says Professor Schützenberger in his introduction to the lecture on my True Atomic Weight: “To him (i. e. Hinrichs), and we may say, somewhat to all of us, the elements of which the material world is composed, are the result of the condensation, according to certain laws, of a single principle, which he (Hinrichs) calls PANTOGEN.” *Actualités*, p. 4; 1896. See dedication, last clause.

4. This is not the place nor the time for a historic exposition of ATOM MECHANICS; but we may state, that by publications and by letters received we could easily show that this change has been mainly due to our own work, a notable part of which is still credited to those who merely appropriated it surreptitiously, as did Naumann, Dana, Lothar Meyer and a few others.

5. This implies that many of the Stasians do not believe in their own statements. It is palpably impossible to admit the Stasian Atomic Weights and at the same time conceive the elements to be compounds of some primitive matter or perhaps a few such materials (if that were not almost equally self-contradictory).

6. Now, we have shown the Stasian Atomic Weights to be erroneous to a much greater extent than necessary to destroy their value as an argument for the complexity of the elements. We have found all well established atomic weights multiples of one twenty-fourth of that of carbon, correspondingly to half the atomic weight of hydrogen. True Atomic Weights, p. 208—213.

7. As to constitution, the elements may be divided into three systems, namely THE HYDROGEN, CARBON AND IRON SYSTEMS. The last two are very comprehensive. They vary in two ways, in valence and in weight. We shall consider each of these variations separately.

8. Let us start with the monad carbon,  $C = 12$ ; and see how it varies in weight. First by simple increase in length, the weight  $\Delta$  and  $2\Delta$  added gives a heavy and a light dyad. See plate, page 80. Here  $\Delta$  is 16. Hence the heavy dyad is Si 28 and the light dyad —? 44. These combinations correspond to binary compounds of elements.

9. Either of these dyads next combines with three, and six and twice six  $\Delta$ , like ternaries (nitrates, chlorates) but under more or less previous surrender of weight to secure complete combination—as H has to be surrendered to make hydrocarbons combine. In the carbon group we have instead of  $3\Delta = 48$  and  $6\Delta = 96$ , only 45 and 89, leaving 3 and 7 for the tie holding the  $\Delta$  together around the dyads.

10. THE CHANGE IN VALENCE is combined with a change in electrical character. Carbon has the valence 4 and is about equally positive and negative. Increase of matter makes it negative and decrease makes it positive. Thus:  $12 + 2 = 14 = N$ ,  $12 + 4 = 16 = O$  and  $12 + 7 = 19 = F$  are increasingly negative and of valence 3, 2, 1 respectively. So  $12 - 1 = 11 = B$ , and subtraction of 2 more gives successively  $9 = Be$  and  $7 = Li$ , the positive elements of valence 3, 2, 1.

11. Between the positive and negative valence One we have long suspected a VALENCE ZERO; our general formula of

1874 (Principles, page 180, 181) and comparison to hydrocarbons paralleled, shows this. This group of elements evidently is represented by argon and helium. For  $a = 2$  ( $10 - n$ ) gives for the valence  $n = 0$ ,  $a = 20$ . We will not now further enlarge on the production of positive and negative electric character by removal and addition of matter to the carbon. See diagram at upper right hand of Plate 80.

12. The iron system corresponds exactly hereto, except that ITS ELECTRICAL CHARACTER IS REVERSED, that is, becomes negative by subtraction of matter. This is already strongly marked in my Programme (1867) in the reversal of the spiral, § 37, p. 9 (see Plate 396) specified in § 54, p. 10.

13. The diagram, Plate 397, gives an ideally complete view of THE COMPOSITION OF THE ELEMENTS. The carbon system (C 12, smaller disks) starts near the center (pantogen) and divides into light (open) and heavy (full disks). The iron system starts farther from the center (Fe = 56, larger disks). The Argonoids and Adamantoids are opposite extremes, joined by the 1, 2, 3 atomic negatives and positives in upper and lower half of diagram.

14. There is of course no such a thing as a real PERIODIC SYSTEM of the elements—consecutive spires of eight elements each, increasing the atomic weight by sixteen for each spire. This is nothing but a hasty generalization from my *Atomechanik* of 1867 on the part of Lothar Meyer. He reviewed my book, condemned it; then published his periodic law. See how Mendeleeff's is only a reflection of mine, top figure, page 398 where A-B represents a vertical, plane mirror. Details, *True Atomic Weights*, pp. 227-255.

15. All about the valencies is given in my Programme (1867, p. 11-17), where also diagram of valencies is given on page 15, here reprinted, page 385. The wall chart (p. 391) has hung for twenty years in my lecture hall in Darkest America; it is the above (plate 396) more carefully drawn. Adapted to letter press, we used diagrams p. 73. Look at that in a mirror, you have the so-called Mendeleeff's, see p. 398.

16. The constitution here given makes it most probable, that when intensely heated in a properly resistant autoclave, DOUBLE DECOMPOSITIONS OF THE ELEMENTS may be produced (True Atomic Weights, p. 224).

Most assuredly, THE CENTRAL PARTS OF THE EARTH consist mainly of the heaviest metals (Au, Pt). The specific gravity of the nucleus must be at least 16 (Plana); hence must consist mainly of these and kindred metals. The physical and chemical properties of the elements are functions of the form and weight of their atoms.

17. At the close of this hasty glance at the chemical composition of the elements, we thus come to ADOPT THE OPINION OF THE ANCIENTS that it is not impossible to convert one element into another, or in the language of the Ancients, to make gold. Hence we have placed the Chrysopoeia of Cleopatra (Berthelot) at the top of page 385 above our old system of valence. Also the Ouroborus on the first page of this book and here at its close.

18. The element atoms are different compounds from those of compound atoms; for in the first the constituent atoms or pantogen atoms are rigidly united, admitting not even of separate vibrations (96, 11). It will accordingly require AN IMMENSE AMOUNT OF ENERGY to effect their decomposition. But whether that is soon effected or not, I think it is now evident that all matter is One which we call Pantogen, and that the Ancients were right in saying: EN TO ΠΑΝ.





# HINRICHS' CONTRIBUTIONS TO ATOM-MECHANICS.

---

PUBLISHED IN THE COMPTES RENDUS OF THE  
ACADEMY OF SCIENCES OF PARIS.

---

## FIRST SERIES.

GENERAL MECHANICS OF THE THREE STATES OF  
AGGREGATION.

1873: Tome 76, p. 1357; p. 1408; p. 1592.

1875: Tome 80, p. 47; p. 565; p. 766.

## SECOND SERIES.

THE GENERAL RELATIONS BETWEEN BOILING POINT,  
PRESSURE AND ATOMIC WEIGHT AND  
FORM OF COMPOUNDS.

1891: Tome 112, p. 998; p. 1127; p. 1436.

1891: Tome 113, p. 36; p. 313; p. 468; p. 500; p. 743,  
p. 798.

## THIRD SERIES.

THE GENERAL MECHANICAL EFFECTS OF CHEMICAL  
SUBSTITUTION.

1892: Tome 114; p. 597; p. 1015; p. 1064; p. 1113; p.  
1272; p. 1367.

1892: Tome 115, p. 177; p. 239; p. 314.

## FOURTH SERIES.

DETERMINATION OF THE TRUE ATOMIC WEIGHT OF  
THE ELEMENTS.

1892: Tome 115, p. 1074.

1893: Tome 116, p. 431; p. 695; p. 753.

1893: Tome 117, p. 663; p. 1075.

1894: Tome 118, p. 528.

---

A reference list to the author's contributions to Cosmical Science, Meteorology and Technical Chemistry has been published elsewhere. The work in Meteorology has been quite voluminous.

**HINRICHS'**  
**SEPARATE WORKS ON ATOM-MECHANICS.**

PROGRAMME DER ATOM-MECHANIK, oder, die Chemie eine Mechanik der Pan-Atome.—44 pp. 4<sup>o</sup>, Iowa City, Iowa, 1867. French Resumé of same, 4 pp. 4<sup>o</sup>, November 1867. English Resume, 4 pp. 4<sup>o</sup>, August 1867.

THE PRINCIPLES OF PURE CRYSTALLOGRAPHY.—pp. IV, 44, in 8<sup>o</sup>, Davenport, 1871. See especially, Chapter VI.

THE METHOD OF QUANTITATIVE INDUCTION IN PHYSICAL SCIENCE.—Davenport, 1872. See especially the last section, p. 36, giving the Mechanics of the three States of Aggregation.

THE PRINCIPLES OF CHEMISTRY AND MOLECULAR MECHANICS.—200 pp., 8<sup>o</sup>, with two plates. Cloth. Davenport and New York, 1874.

BEITRAEGE ZUR DYNAMIK DES CHEMISCHEN MOLEKUELS.—Leipzig, Gustav Fock, 1892:

I.—The Molecule as a System of Material Points. II.—The Energy of the Molecule. III.—Graphical Structural Formulæ. IV.—The Moments of Inertia of the Molecules. VI.—The Boiling Points of Isomeric Bodies Determined by the Moment of Inertia of the Molecules.

The above Beitraege will be sent by the undersigned on receipt of 50 cents.

These Beitraege were sent to A. W. Hofmann for the DEUTSCHE CHEMISCHE GESELLSCHAFT (I, II, April, 1872; III—VI, April, 1873), of which the author was a Foreign Member.

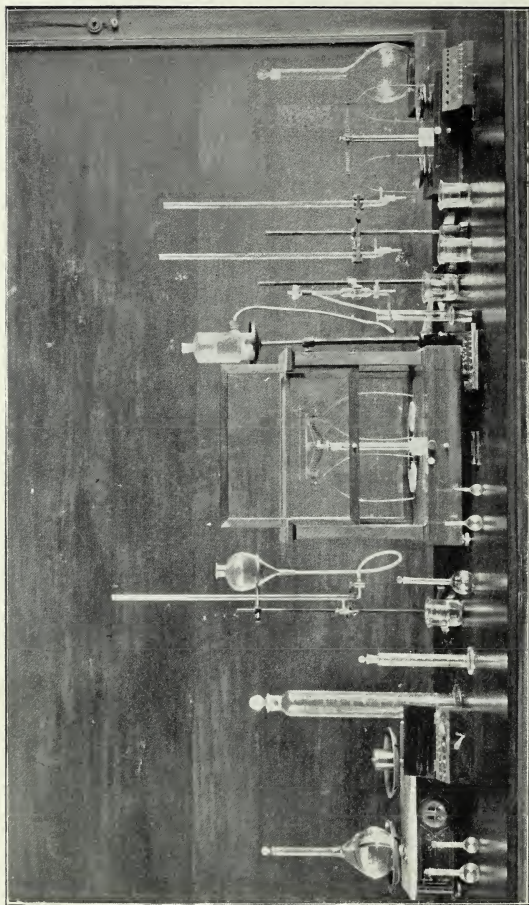
No one at Berlin did understand these papers. This very interesting and characteristic episode in the history of Atom-Mechanics is contained in the above edition of 1892.

---

THE TRUE ATOMIC WEIGHTS of the Chemical Elements and the Unity of Matter. With Plates and Diagrams. St. Louis: Carl Gustav Hinrichs, Publisher. B. Westermans & Co., New York. 1894. XVI and 256 pp. 8 vo. Will be sent prepaid to any part of the Postal Union upon receipt of price (\$3.00) by the publisher.

Address **CARL GUSTAV HINRICHS, Publisher,**  
ST. LOUIS, MO., U. S. A.

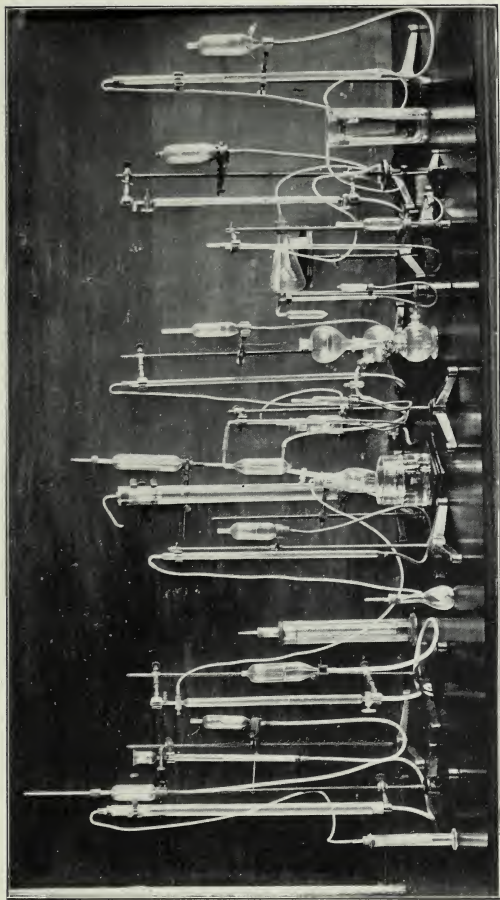




LECTURE 2.

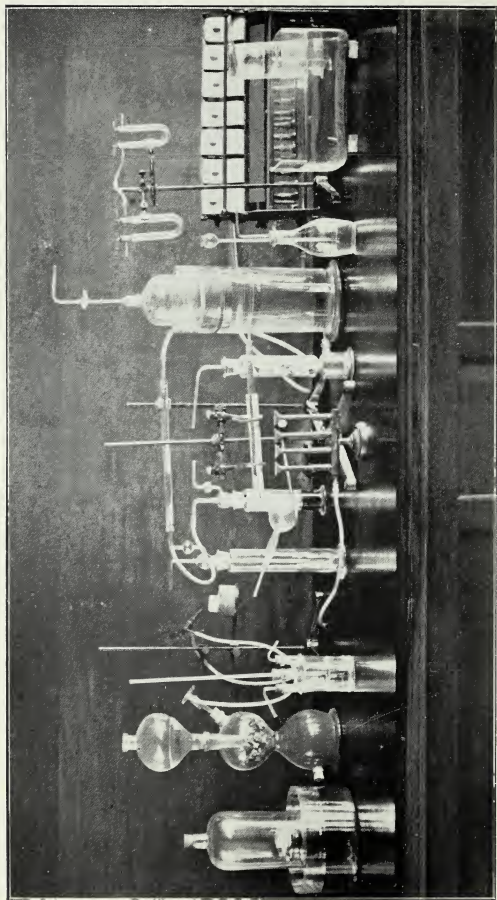
## WEIGHT AND MEASURE.

LECTURES 46, 50.



LECTURE 49.

GASOMETRIC APPARATUS.

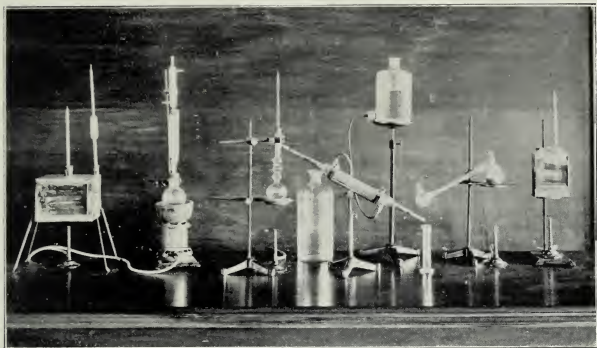


LECTURES 16, 17.

GAS MANIPULATION.

LECTURES 30, 32.

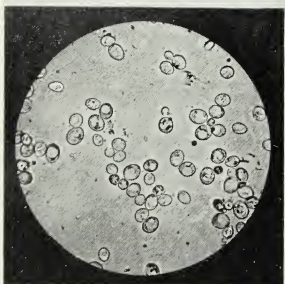
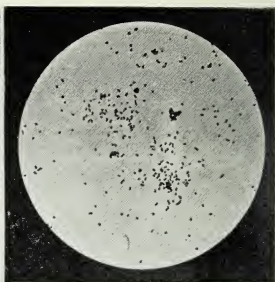




DISTILLING AND EXTRACTION APPARATUS.



PROFESSOR'S STAND IN THE CHEMICAL LABORATORY,  
ST. LOUIS COLLEGE OF PHARMACY.



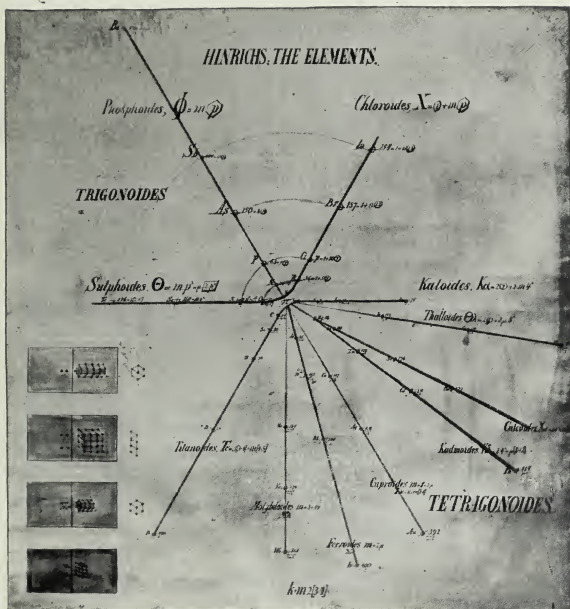
## MICROGRAPHS OF FERMENTS.

LECTURE 71.

SACCHAROMYCES—  
-CEREVISIÆ, YOUNG.  
" OLD.

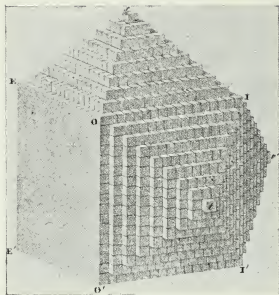
BACILLUS—  
-ACETICUS.  
-ACIDI LACTICI.



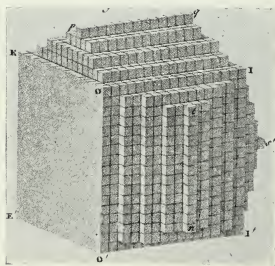


HINRICHS, THE ELEMENTS. 1867.

WALL CHART.



THE DODECAHEDRON.

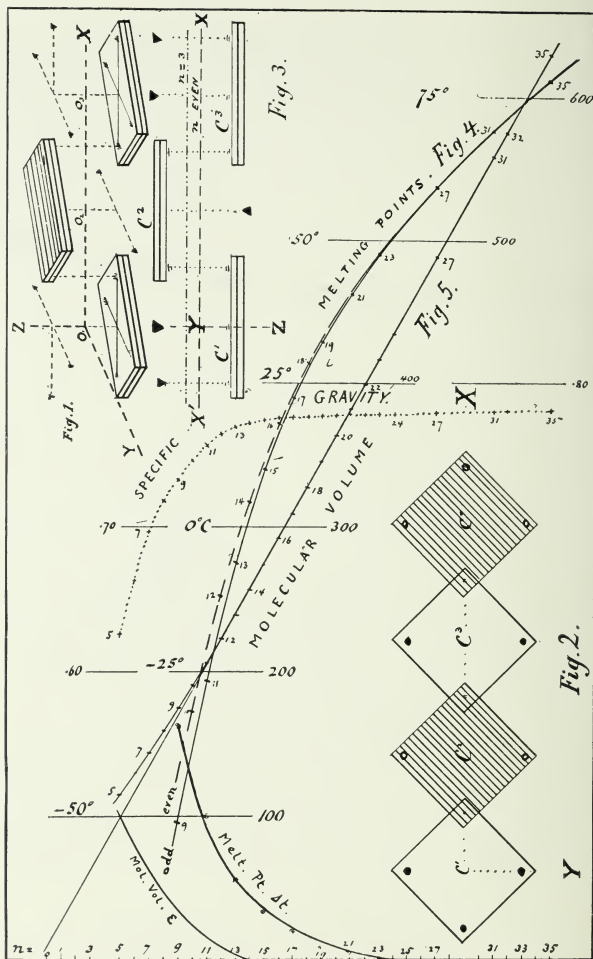


THE PYRITOHEDRON.

HAUY, ORIGIN OF SECONDARY FORMS.

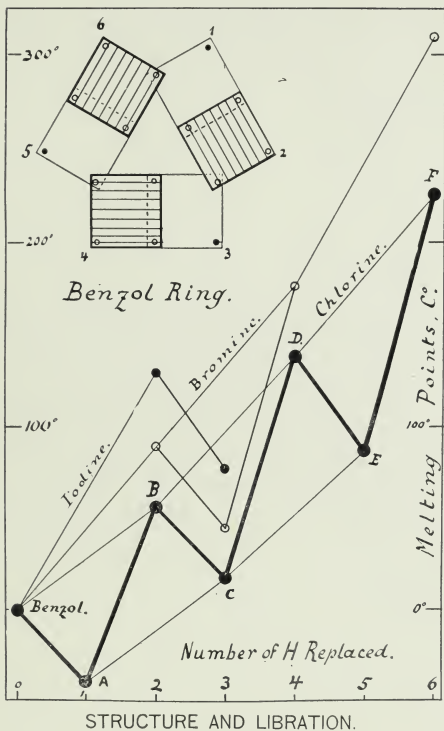


agré, cher et honore homme, l'assurance de  
ma amitié et de ma très haute estime et la plus sympathique de  
Dauvergne



# STRUCTURE AND PROPERTIES.

THE PARAFFINS.

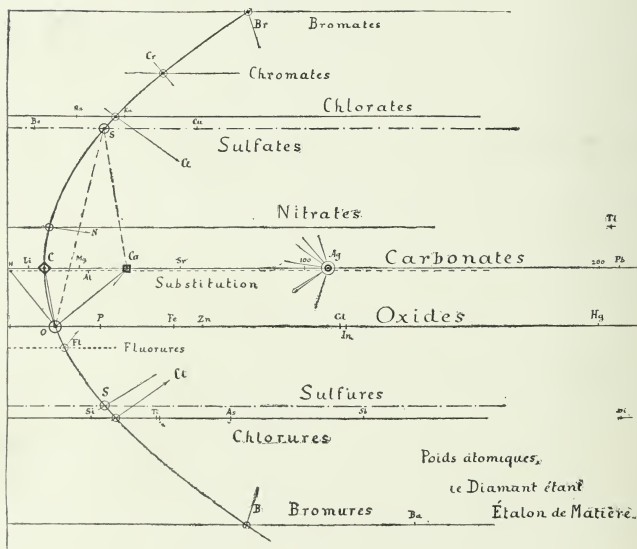
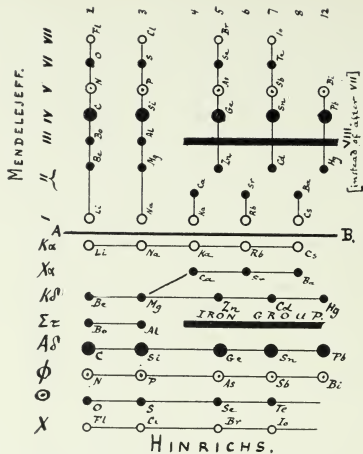


BENZOL.





HINRICHS, SYSTEM OF THE ELEMENTS, 1897.



ATOMIC WEIGHT, DIAMOND STANDARD.



nach einer ausgewählten Darstellungsmethode des Anatas, Bismut und  
 Arsen.

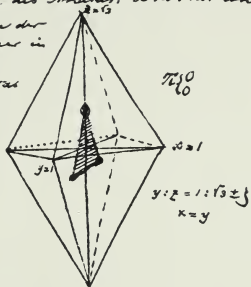
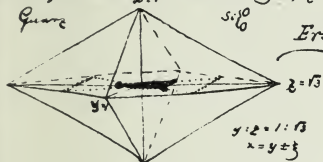
298~ Übersicht der Formen, mit Angabe der  
 Stellung des Dreiecks  $R_1^0$  im Kristall, dieses in  
 seiner konventionellen Stellung gezeichnet.

Quarz

$S_1^0$

Anatas

Erste Form



$x = 6$

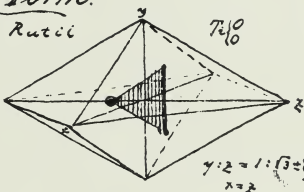
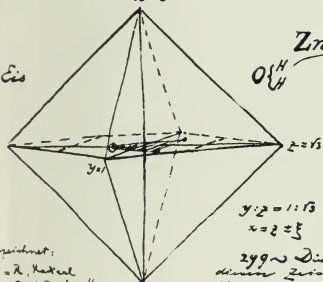
Zweite Form

Eis

$O_1^H$

Rutil

$T_1^0$



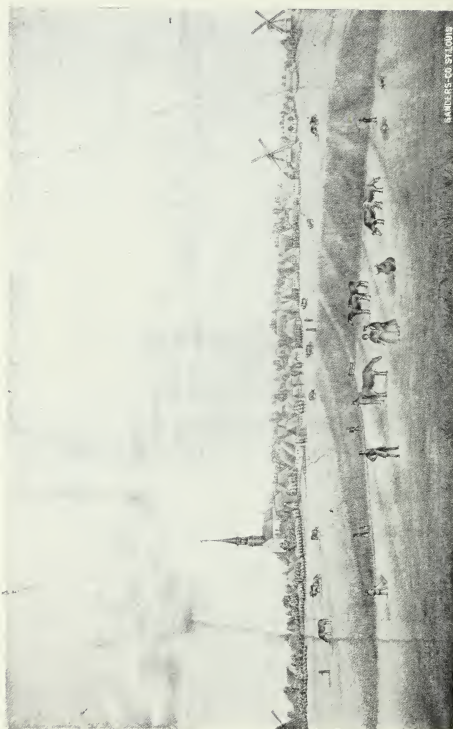
$y:z = 1:\sqrt{3}$   
 $x = y \pm \frac{1}{2}$

$y:z = 1:\sqrt{3}$   
 $x = z$

gezeichnet:  
 $\odot = R$ , Rutil  
 $\circ = Q$  (D oder H)

299~ Die Volumen-Verhältnisse kommen in  
 diesen Zeichnungen nicht wohl beachtet werden.  
 Sie stellen die Formen in den konventionellen  
 kristallographischen Einheiten dar. Nennen

HALF OF PAGE 34 FROM  
 HINRICHS' PROGRAMME DER ATOMECHANIK, 1867.



1843.

# A LOOK-OUT TO THE OLD PASTURES (67, 1).

Lunden was the chief town of North Ditmarsia, the little Republic between Eyder, Elbe and North Sea that maintained its independence for centuries, and kept itself free from all feudal institutions.











UNIVERSITY OF ILLINOIS-URBANA



3 0112 068477543